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Nanoclusters in Catalysis: A Comparison of CS_2 Catalyst Poisoning of Polyoxoanion- and Tetrabutylammonium-Stabilized 40 ± 6 Å Rh(0) Nanoclusters to 5% Rh/Al_2O_3, Including an Analysis of the Literature Related to the CS_2 to Metal Stoichiometry Issue

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It is crucial in metal particle catalysis to know the true number of catalytically active surface sites; without this knowledge it is impossible (i) to know the true turnover frequency (TOF, i.e., the moles of product/(moles of active metal atoms × time)); (ii) to know for certain whether a (quantitatively) better catalyst has been made—*on a per-active-metal-atom basis*; (iii) to know the amount of active sites remaining in a deactivated catalyst; and (iv) to know how many active sites have been regenerated in a reactivated catalyst. For this reason, herein we report the first quantitative, more complete and fundamental study of *nanocluster catalyst poisoning* using the preferred CS_2 method with polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters; 5% Rh/Al_2O_3 is also examined as a valuable comparison point. Both catalysts are examined under essentially identical conditions and while catalyzing a prototype reaction, cyclohexene hydrogenation. A number of control studies are also reported to be sure that the kinetic method used to follow the CS_2 poisoned hydrogenation reaction is reliable, to test for H_2 gas-to-solution mass-transfer limitations, to test for reversibility in the CS_2 poisoning, and to test for loss of the volatile CS_2. The results allow 10 previously unavailable insights and conclusions, including the first quantitative comparison of the active-site corrected TOF for a nanocluster catalyst (in this case Rh(0) nanoclusters) to its supported heterogeneous counterpart (the 5% Rh(0) on Al_2O_3). *The results show that the nanocluster surface Rh(0) is between 2.3 and 23 times more active on a per-active-metal-atom basis.* Overall, the results introduce to the transition-metal nanocluster area the catalyst poisoning methodology necessary for the determination of the number of *active* metal sites. The important literature of CS_2 catalyst poisoning studies is also cited and discussed with a focus on the previously neglected issue of the exact poison/metal stoichiometry ratio. Significantly, the single metal crystal plus CS_2 literature provides evidence that the CS_2/metal ratio probably lies between 1/1.5 and 1/10 in most cases. The data presented herein suggest that the CS_2/Rh ratio for the Rh(0) nanoclusters is very likely within this range and for certain is <1/17.

Introduction

Recently, there has been considerable interest in the synthesis, characterization, and application of nanoclusters,[1] that is, particles which have diameters of ≤10 nm (100 Å).[2,3] One application of transition-metal nanoclusters is in catalysis, where such small metal particles may serve as "soluble analogues of heterogeneous catalysts." [2]

Previously we reported the synthesis and characterization of polyoxoanion- and tetrabutylammonium-stabilized Ir(0)[4,5]

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(1) (a) Schmid, G.; Bäumle, M.; Geerkens, M.; Heim, I.; Osemann, C.; Sawitowski, T. *Chem. Soc. Rev.* **1999**, *28*, 179−185. (b) *Clusters and Colloids; From Theory to Applications*; Schmid, G., Ed.; VCH: New York, 1994. (c) *Active Metals: Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH: Weinheim, 1996. (d) *Physics and Chemistry of Metal Cluster Compounds*; de Jongh, L. J., Ed.; Kluwer Academic Publishers: Dordrecht, 1994; Vol. 18. (e) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709−1727.

(2) Aiken, J. D., III; Lin, Y.; Finke, R. G. *J. Mol. Catal. A: Chem.* **1996**, *114*, 29−51.

(3) Aiken, J. D., III; Finke, R. G. *J. Mol. Catal. A: Chem.* **1999**, *145*, 1−44.

(4) (a) Lin, Y.; Finke, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 8335−8353. (b) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382−10400. (c) Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, *9*, 3083−3095.

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and Rh(0)[6] nanoclusters. The Rh(0) nanoclusters, synthesized from the polyoxoanion complex $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]$, **1** (1,5-COD = 1,5-cyclooctadiene)[7] have been shown to be long-lived catalysts in solution, exhibiting ≥193 000 total turnovers for cyclohexene hydrogenation, a lifetime which approaches that of a commercially available 5% Rh/Al_2O_3 heterogeneous catalyst tested under identical conditions as part of the same study.[8]

A determination of the percentage of *surface, catalytically active* metal atoms in the Rh(0) nanocluster catalyst is an important but largely undetermined value for nanocluster catalysts (vide infra). In addition, it is also of considerable interest to compare the number of catalytically active sites for the Rh(0) nanoclusters to those for a "traditional" heterogeneous catalyst such as 5% Rh/Al_2O_3: does such a determination support or refute the developing analogy of nanoclusters as "soluble analogs of heterogeneous catalysts"? [2,3] The comparison of these two catalysts should prove interesting since each material has quite similar numbers of exposed surface atoms, 33% for 5% Rh/Al_2O_3 as determined by chemisorption measurements, and 28−34% for Rh(0) nanoclusters as estimated for idealized, spherical ccp Rh(0) nanoparticles of 40 ± 6 Å diameters.[9]

For the 5% Rh/Al_2O_3 case, the percentage of *exposed metal atoms* can easily be determined by CO or H_2 chemisorption analysis; however, the number of exposed metal atoms determined by chemisorption experiments in the *solid state* is not necessarily equivalent to the number of catalytically active surface sites *in solution*.[10] The expected effects of anionic and cationic stabilizers, as well as solvent, adsorbed onto the surfaces of dried, solid-state samples of nanoclusters are another problematic issue of at least solid-state chemisorption measurements—one reason why the recent studies of Bradley and co-workers, measuring CO chemistorption on nanoclusters *in solution*, are significant.[11] We sought, therefore, to (a) develop further the needed quantitative, solution-based catalyst poisoning methods, and then (b) use those methods to establish the number of catalytically active metal atoms in both the Rh(0) nanocluster system and the classical Rh(0) heterogeneous catalyst system.

Quantitative poisoning studies of *heterogeneous* catalysts are well-known and can employ a range of poison types: [10,12−15] S-based (CS_2, RSH or RS^-, PhSH or PhS^-, H_2S or HS^-, thiophene, Me_2S, SCN^-, RCS_2^- (see elsewhere)[16]), N-based (pyridine, H_3N, $R_{3-x}H_xN$), P-based (PR_3), C-based (CO, CN^-), O-based (O_2^-, OH^-, RO^-), or other-element-based poisons (Sb, Se, Te, Hg, Pb, Bi, Cd, Cu, and Zn). However, poisons that contain sulfur are the most common and are arguably the most studied since sulfur compounds are known impurities in fuels and petroleum-based feedstocks.[17] The arguably preferred S-poison based on the prior literature is CS_2;[10,14,15,18] hence, solution-phase CS_2 poisoning studies became the focus of the present studies.

Even with preferred poisons such as CS_2, one needs to appreciate that studies on single crystals and heterogeneous catalysts reveal that the poisoning of metal surfaces by S *is complex* with either steric (ensemble)[17a,19] or electronic (ligand)[17a,20,21] effects often being discussed. Although steric effects are generally local and can be minimized with the use of "small" poisons such as H_2S and CS_2, electronic perturbations of the surface appear to be long-range in nature and have been used to explain poison/metal-atom stoichiometry ratios seen in studies of single crystals of *anywhere from 1/1.5 to 1/20* (results that we will examine in more detail in the Discussion section; vide infra).[22,23] In addition to steric and electronic effects, poison studies are further complicated by possible poison-induced morphological changes in the catalyst, that can then alter its activity.[17a,24] Hence, as

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(6) Aiken, J. D., III; Finke, R. G. *Chem. Mater.* **1999**, *11*, 1035−1047.

(7) The synthesis and characterization of $(1,5\text{-}COD)M \cdot P_2W_{15}Nb_3O_{62}{}^{8-}$: (a) Nomiya, K.; Pohl, M.; Mizuno, N.; Lyon, D. K.; Finke, R. G. *Inorg. Synth.* **1997**, *31*, 186−201. (b) Pohl, M.; Lyon, D. K.; Mizuno, N.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 1413−1429. (c) Pohl, M.; Finke, R. G. *Organometallics* **1993**, *12*, 1453−1457. (d) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Sur, S.; Mizuno, N. *Inorg. Chem.* **1990**, *29*, 1784−1787. (e) See also refs 51a−d.

(8) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8803−8810.

(9) The number of metal atoms, *y*, per *n*th shell, in full shell, "magic number" clusters is given by the equation $y = 10n^2 + 2$ ($n > 0$). See: Schmid, G. *Endeavour, New Ser.* **1990**, *14*, 172−178.

(10) The introduction to the following paper is classic: "The problem of determining the number of active centers on a catalytic surface and the activity of each center is crucial in experimental catalytic investigations. It has a long history". Gonzalez-Tejuca, L.; Aika, K.; Namba, S.; Turkevich, J. *J. Phys. Chem.* **1977**, *81*, 1399−1406.

(11) (a) For a recent development of the precise differential pressure measurement methods for H_2 chemisorption measurements in solution on 2.5 nm Rh(0) nanoparticles stabilized by PVP, see: Bradley, J. S.; Busser, W. *Catal. Lett.* **1999**, *63*, 127−130. (b) Note, however, that for the poisoning studies herein, as well as with all of the analogous heterogeneous catalysis chemisorption and poisoning studies, there is still the issue of the exact ligand (H_2; CO; CS_2; etc.) to metal stoichiometry ratio required to poison a single active site (e.g., see ref 30), a value that is needed to determine the absolute number of active sites.

(12) Maxted, E. B. *Adv. Catal.* **1951**, *3*, 129−178.

(13) Butt, J. B. *Catal. Sci. Technol.* **1987**, *6*, 1−63.

(14) (a) Fengyi, L.; Shibiao, C.; Jianhui, L. *J. Alloys Compd.* **1992**, *181*, 457−462. (b) Chen, S.-Y.; McCoy, B. J.; Smith, J. M. *AIChE J.* **1986**, *32*, 2056−2066.

(15) Notheisz, F.; Zsigmond, Á.; Bartók, M.; Szegletes, Z.; Smith, G. V. *Appl. Catal., A* **1994**, *120*, 105−114.

(16) (a) There is but a single prior report of quantitative poisoning studies of nanoclusters in solution: Moiseev and co-workers' use of poisons such as C_2H_5SH, KSCN, and Et_2NCS_2Na to deactivate their now classic $Pd_{\sim560}phen_{\sim60}(PF_6)_{\sim60}O_{\sim60}$ catalysts for ethylene and propylene oxidation (more bulky ligands such as PPh_3 or phenanthroline proved to be ineffective poisons).[16b] They report that 15 and 50 sulfur-based poison molecules are required to completely poison the $Pd_{\sim560}$ surface to the oxidation of C_3H_6 and C_2H_4, respectively. The only other reported example of a solution-based soluble nanocluster poisoning study is our own demonstration that ≤0.2 equiv of PPh_3 completely shut down the cyclohexene hydrogenation activity of polyoxoanion-stabilized Ir(0) nanoclusters.[5] (b) Vargaftik, M. N.; Zargorodnikov, V. P.; Stolarov, I. P.; Moiseev, I. I.; Kochubey, D. I.; Likholobov, V. A.; Chuvilin, A. L.; Zamaraev, K. I. *J. Mol. Catal.* **1989**, *53*, 315−348.

(17) (a) Rodriquez, J. A.; Hrbek, J. *Acc. Chem. Res.* **1999**, *32*, 719−728. (b) Friend, C. M.; Chen, D. A. *Polyhedron* **1997**, *16*, 3165−3175.

(18) (a) Palinko, I. *Stud. Surf. Sci. Catal.* **1994**, *88*, 603−608. (b) Chen, S.-Y.; Smith, J. M.; McCoy, B. J. *J. Catal.* **1986**, *102*, 365−376. (c) Kishida, S.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 270−272.

(19) Zhang, C. J.; Hu, P.; Lee, M.-H. *Surf. Sci.* **1999**, *432*, 305−315.

(20) Oudar, J. *Stud. Surf. Sci. Chem.* **1982**, *11*, 255−268.

(21) Feibelman, P. J.; Hamann, D. R. *Phys. Rev. Lett.* **1984**, *52*, 61−64.

(22) (a) Goodman, D. W. *Appl. Surf. Sci.* **1984**, *19*, 1−13. (b) Goodman, D. W.; Kiskinova, M. *Surf. Sci.* **1981**, *105*, L265−L270. (c) Goodman, D. W.; Kelley, R. D.; Madey, T. E.; Yates, J. T., Jr. *J. Catal.* **1980**, *63*, 226−234.

(23) Oudar, J.; Pinol, S.; Pradier, C. M.; Berthier, Y. *J. Catal.* **1987**, *107*, 445−450.

(24) Chang, J.-R.; Chang, S.-L.; Lin, T.-B. *J. Catal.* **1997**, *169*, 338−346.

with any indirect method there is the issue of whether or not the method (in this case the poison) is "reporting, or causing, the news." It is also important to appreciate that the catalyst poisoning literature makes it clear that poison-to-metal ratios are *not absolute* but, rather, depend upon the other ligands that are present, the reaction, the pressure, the temperature, and the other experimental conditions.[12-24] Nevertheless, despite the drawbacks in catalyst poisoning studies, catalysis is inherently a completely kinetic phenomenon so that *catalyst poisoning kinetics are an essential component of any study that aspires to establish the true number of active sites or any property connected to this value such as the turnover frequency (TOF) or total turnovers (TTOs)*.[10]

Despite the importance of knowing the number of active surface metal atoms in *any* catalyst and despite the central position of poisoning kinetics in such research, there is no separate, full paper study of nanocluster poisoning,[25] no selection of a preferred poison for such studies, nor has any analysis of the weaknesses and strengths of the catalyst poisoning method appeared in the nanocluster literature[16] prior to the present contribution—all despite the fundamental importance of such studies. It is important to note that such poisoning experiments should be done in each and every study employing nanoclusters (or for that matter any other material) in catalysis. Such a determination of the number of active sites in the nanocluster catalyst, and for each catalytic reaction investigated, is central: (i) to know the true turnover frequency (TOF, i.e., the moles of product/(moles of active metal atoms × time)); (ii) to know for certain whether or not a (quantitatively) better catalyst has been made—*on a per-active-metal-atom basis*; (iii) to know the amount of active sites remaining in a deactivated catalyst; and (iv) to know how many active sites have been regenerated in a reactivated catalyst. These are all points well-known in heterogeneous catalysis since Boudart's pioneering work emphasizing the importance of the TOF in metal particle catalysis.[26] Consistent with the above points, it is easy to pick papers from the current nanocluster literature where the application of the CS_2 methods reported herein should have been used (i.e., had the present methods been available) to support, or refute, the main conclusions of those often very interesting studies.[27,28] In short, the poisoning methods and the specific use of CS_2 studied in the present paper promise to be of broader significance to the area of nanocluster catalysis just as such studies have proven important to the area of heterogeneous catalysis.

Herein we report quantitative catalyst poisoning experiments using CS_2 for both polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters and for 5% Rh/Al_2O_3, both while catalyzing a prototypical structure-insensitive reaction,[29] cyclohexene hydrogenation. These studies were accomplished using an initial-rate method that follows the hydrogen pressure loss over time, but were also checked with control experiments employing a second and direct, although less precise, ^{1}H NMR method. The specific goals of the poisoning studies which follow are (a) to determine the percentage of catalytically active metal atoms on the surface of both the Rh(0) nanoclusters and an analogous 5% Rh(0)/Al_2O_3 heterogeneous catalyst; (b) to look in detail at the literature of what at least appears to be the Achilles heel of the otherwise powerful method of catalyst poisoning studies, the unknown exact poison/metal atom stoichiometry ratio; (c) to make a direct comparison of the activity of the two Rh(0) catalysts on a more rigorous, per-metal-atom basis (and since the unknown poison/metal stoichiometry ratio tends to cancel out of such comparisons); and (d) to bring the preferred poison, carbon disulfide,[14,15,18] and solution-phase catalyst poisoning studies into the nanocluster area for the first time.

Results

1. Chemisorption Analysis of the 5% Rh/Al_2O_3. The 5% Rh/Al_2O_3 catalyst was analyzed by H_2 and CO chemisorption to determine the percentage of exposed Rh metal atoms.[30] The analyses were in excellent agreement showing that ca. 33% of the *total* Rh metal atoms are exposed (H_2 chemisorption, 33.4 ± 0.6% exposed; CO chemisorption, 32.4 ± 0.5% exposed). In short, the 5% Rh(0)/Al_2O_3 heterogeneous catalyst appears to be an excellent choice for comparison to the Rh(0) nanocluster catalysts, since each has a similar apparent (average) number of surface Rh(0) atoms.[31] Consistent with this and as a further check, a TEM

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(25) Studies are available which make corrections based on the number of exposed metal atoms.[25a,b] Even those studies are rare, however: (a) Bönnemann, H.; Wittholt, W.; Jentsch, J. D.; Tilling, A. S. *New J. Chem.* **1998**, *22*, 713−717. (b) Bönnemann, H.; Brijoux, W.; Siepen, K.; Hormes, J.; Franke, R.; Pollmann, J.; Rothe, J. *Appl. Organomet. Chem.* **1997**, *11*, 783−796.

(26) Boudart, M. *Chem. Rev.* **1995**, *95*, 661−666. Boudart, M. *J. Mol. Catal.* **1985**, *30*, 27.

(27) (a) Hwang, C. B.; Fu, Y. S.; Lu, Y. L.; Jang, S. W.; Chou, P. T.; Wang, C. R. C.; Yu, S. J. *J. Catal.* **2000**, *195*, 336−341. (b) Crooks, R. M.; Chechik, V. *J. Am. Chem. Soc.* **2000**, *122*, 1243−1244. (c) Schmid, G.; Maihack, V.; Lantermann, F.; Peschel, S. *J. Chem. Soc., Dalton Trans.* **1996**, 589−595. (d) Wang, Y.; Liu, H.; Jiang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1878−1879. (e) Shiraishi, Y.; Nakayama, M.; Takagi, E.; Tominaga, T.; Toshima, N. *Inorg. Chim. Acta* **2000**, *300−302*, 964. See p 968 where the activity of commercial Pt black is claimed, without correction for the relative number of active sites, to be "much less than that of PVP-protected Pt nanoclusters". (f) Li, Y.; El-Sayed, M. A. *J. Phys. Chem. B* **2001**, *105*, 8938. (g) Klingelhöfer, S.; Heitz, S.; Greiner, W.; Oestreich, A.; Föster, S.; Antonietti, M. *J. Am. Chem. Soc.* **1997**, *119*, 10116. (h) Toshima, N. *Macromol. Symp.* **2000**, *156*, 45. Note that the conclusion on p 50, that "the high catalytic activity (of Pt(core)/Pd(surface) heterobimetallic nanoclusters) can be explained by the electronic effect of neighboring Pt on the surface Pd", does not follow without poisoning studies to rule out the simple alternative hypothesis that the Pt may have increased the number of Pd active sites. (i) Toshima, N.; Shiraish, Y.; Teranishi, T.; Miyake, M.; Tominaga, T.; Watanabe, H.; Brijoux, W.; Bönneman, H.; Schmid, G. *Appl. Organomet. Chem.* **2001**, *15*, 178−196. See Figure 16 where a correction is needed for the number of active sites in this activity vs average particle diameter plot. (j) Siepen, K.; Bönneman, H.; Brijoux, W.; Rothe, J.; Hormes, J. *Appl. Organomet. Chem.* **2000**, *14*, 549−556. A determination of the number of active sites vs the different Pt/Rh percentages in the Pt/Rh bimetallic nanocluster is needed—is the number of active sites a maximum at the most active 10% Pt/90% Rh composition?

(28) (a) Köhler, J. U.; Bradley, J. S. *Langmuir* **1998**, *14*, 2730−2735. (b) Le Bars, J. L.; Specht, U.; Bradley, J. S.; Blackmond, D. G. *Langmuir* **1999**, *15*, 7621. Note the high total turnovers, turnover frequencies, and evidence for high activity from low coordination number active sites in this valuable paper.

(29) Gates, B. C. *Catalytic Chemistry*; John Wiley: New York, 1992; p 387.

of the 5% Rh/Al_2O_3 catalyst revealed that at least the discrete, countable Rh(0) particles in the 5% Rh/Al_2O_3 catalyst are 36 ± 18 Å (±50%; Supporting Information, Figure A), in the general size range of our soluble, but 3-fold narrower size distribution, Rh(0) nanoclusters, 40 ± 6 Å (±15%).[6,32] Note, however, as discussed with Figure A, the heterogeneity of the metal particles and agglomerates present in the 5% Rh/Al_2O_3 catalyst (e.g., as visualized by TEM) means that the actual range of particle sizes is broader than indicated by the 36 ± 18 Å value given above.

2. Quantitative CS_2 Poisoning of 5% Rh/Al_2O_3. Reflection revealed that the well-established 5% Rh/Al_2O_3 catalyst was the best starting point for an initial series of experiments using CS_2 as a poison. Once the initial catalytic activity of the unpoisoned heterogeneous catalyst was measured ($\{-dH_2/dt\}_i = 52 \pm 3$ psig/h), separate reaction solutions were prepared and preselected amounts of a 3.32×10^{-5} M CS_2 solution were added under a constant flow of hydrogen. These experiments address the following questions: Does this method work in our hands and for an established catalyst? Are linear or nonlinear poison plots[12-16] seen? What pitfalls need to be avoided during the Rh(0) nanocluster poisoning experiments?

A. Initial-Rate Method. A constant amount of 5% Rh/Al_2O_3, acetone, and cyclohexene, plus a systematically varying amount of a freshly prepared CS_2 solution, were added to the pressurizable Fischer−Porter reaction vessel. In each experiment, the hydrogen pressure was set to 40 ± 1 psig and pressure vs time data were collected for 1 h using our previously described computer-interfaced pressure transducer.[4,5] The initial rate of cyclohexene hydrogenation was then determined from the corrected H_2 pressure vs time data by the methods detailed in the Experimental Section. Plots of pressure vs time data are provided in Figure B of the Supporting Information. Note that the initial rate and the kinetic data from the pressure transducer are, by design, (i) quite precise (±0.1 psig) and (ii) free from the complexities of the exact rate law if the initial conditions are kept the same in each series of experiments (e.g., the initial-rate method avoids the need to establish the dependence of the rate law on the olefin or H_2). The data suggest, by the way, that, for both the 5% Rh/Al_2O_3 catalyst and the Rh(0) nanoclusters, the rate law is zero-order in cyclohexene under the specified conditions; see the Experimental Section.

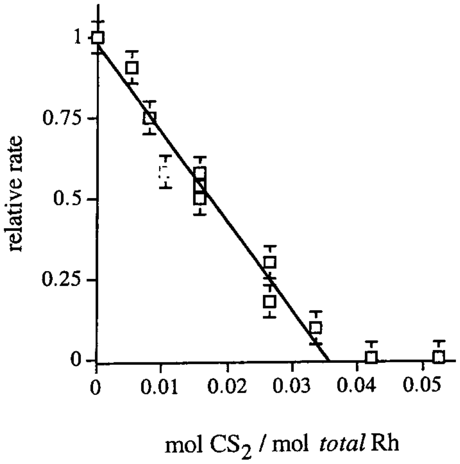

Figure 1. Plot of relative rate vs moles of CS_2/moles of *total* Rh for the hydrogenation of cyclohexene by 5% Rh/Al_2O_3. Rates were determined by the initial-rate method from H_2 pressure vs time data taken over the course of 1 h (Figure B, Supporting Information); the $x_{intercept}$ is 0.035 ± 0.004 mol of CS_2/mol of *total* Rh.

A control experiment was carried out to be sure that the observed reaction rates were not complicated by slow H_2 gas-to-solution, mass-transfer limitations (MTL). The results in Figure C of the Supporting Information show that doubling the concentration of Rh catalyst doubles the initial rate of the reaction; this demonstrates one crucial, up-front requirement for catalyst poisoning (as well as any other chemical-kinetic) studies: that mass-transfer limitations do not occur under the chosen reaction conditions. The absence of MTL effects is further supported by the linearity of the poison plots discussed below.[15]

Another set of control experiments revealed that the CS_2/acetone solutions must be prepared fresh each day to obtain consistent results. Experiments carried out with 1 day old CS_2/acetone solutions resulted in rates that differed by a factor of 3 from those obtained with fresh solutions; see the Supporting Information, Figure D. In light of these results, it is apparent that maintaining the integrity of the CS_2 solutions is critical for collection of accurate catalyst poisoning data; however, this detail is not mentioned in prior solution-phase poisoning studies.[14b,15,18]

Figure 1 shows the results from 12 independent experiments, Figure B, Supporting Information, plotted as the relative rate vs the moles of CS_2/moles of *total* Rh. Linear poison plots, such as the one in Figure 1, have been reported in the literature and are readily described by a simple line, eq 1,[12,33] where y is the relative rate, $-m$ is the slope of the line ($m > 0$), and x is the moles of CS_2/moles of *total* Rh.

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(30) (a) Note that stoichiometric factors of 2 for H/Rh and 1 for CO/Rh were assumed in the chemisorption analysis, an assumption justified ex post facto by the good agreement (33% exposed Rh metal) using these assumptions. However, we note that there are reports in the literature of higher stoichiometric factors of CO/Rh = 1.94 for 1% Rh/SiO_2 (the H/Rh value was 1.84, that is, close to 2.0). Ichikawa, S. *J. Chem. Soc., Chem. Commun.* **1989**, 403−405. (b) In addition, others show that in the H_2 and CO chemisorption analysis of Ir/Al_2O_3, the H/Ir ratio varies from 1.14 to 2.10 and the CO/Ir ratio varies from 0.84 to 1.78, a variation that is dependent upon the percent metal loading in the sample. McVicker, G. B.; Baker, R. T. K.; Garten, R. L.; Kugler, E. L. *J. Catal.* **1980**, *65*, 207−220.

(31) There is, however, a difference between the number of *exposed* atoms on the surface that chemisorption measures and the *total number of atoms* on the surface that is attainable from the average size of the nanoclusters, for example. Only recently have chemisorption measurements on nanoclusters been reported. Bradley and co-workers' recent studies,[11a] as well as their earlier work adding CO to large metal nanocolloids and nanoclusters, show that it is possible to do H_2 (and maybe CO) chemisorption measurements on nanoclusters. However, problems with specific cases can be anticipated; for example with CO and Rh clusters, roughly similar Rh−Rh ($D_{Rh-Rh} \cong 39$ kcal/mol) and Rh−CO ($D_{Rh-CO} \cong 27$ kcal/mol) bond energies[31b] are why too much CO will fragment the clusters, even to mononuclear $Rh(CO)_2$ species[31c] as in the case of supported Rh clusters at sufficiently high CO pressures. (a) Bradley, J. S.; Millar, J. M.; Hill, E. W.; Behal, S. *J. Catal.* **1991**, *129*, 530−539. Rodriguez, A.; Amiens, C.; Chaudret, B.; Casanove, M.−J.; Lecante, P.; Bradley, J. S. *Chem. Mater.* **1996**, *8*, 1978−1986. (b) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1980**, *19*, 896−903. (c) Nagata, T.; Pohl, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1997**, *36*, 1366−1377 and references therein.

(32) Aiken, J. D., III; Finke, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 9545−9554.

$$y = -mx + y_{\text{intercept}} \qquad (1)$$

The amount of CS_2 required to completely poison the catalyst is indicated by the intersection of the poison plot with the x-axis, that is, at $y = 0$.[12,18a] To determine the value of the $x_{\text{intercept}}$, a linear regression analysis of the experimental data was carried out, and the resulting slope and $y_{\text{intercept}}$ were used to calculate the $x_{\text{intercept}}$ from eq 2 obtained when $y = 0$.

$$x_{\text{intercept}} = y_{\text{intercept}}/m \qquad (2)$$

The $x_{\text{intercept}}$ of the plot in Figure 1 is 0.035 ± 0.004 mol of CS_2/mol of *total* Rh metal present ($y_{\text{intercept}} = 0.98 \pm 0.04$ and $m = 28 \pm 2$). Restated, only 3.5 mol % of CS_2 is sufficient to poison completely all of the available active sites in the 5% Rh/Al_2O_3 catalyst.

B. ^{1}H NMR Method. ^{1}H NMR was investigated as a second, albeit less precise, method to check the amount of CS_2 required to poison the exposed Rh(0) atoms in 5% Rh/Al_2O_3. Despite problems traceable to the lower precision of the otherwise desirable, direct ^{1}H NMR method and, therefore, problems following the rates of slow, partially poisoned catalysts, a rough estimate of ~0.03 mol of CS_2/mol of *total* Rh to completely poison the catalyst was obtained (see Figures E and F of the Supporting Information for plots of the data and for a more detailed discussion of the results). That is, the value obtained by the semiquantitative ^{1}H NMR experiment is within experimental error of the 0.035 value obtained by the more precise, and thus recommended, initial-rate method.

3. Quantitative CS_2 Poisoning of Polyoxoanion-Stabilized Rh(0) Nanoclusters. Several independent cyclohexene hydrogenation experiments were performed using the initial-rate method described above to determine the amount of CS_2 required to deactivate the polyoxoanion-stabilized Rh(0) nanoclusters toward cyclohexene hydrogenation. Pressure vs time data are given in Figure G of the Supporting Information.

To begin, each reaction solution was prepared from a stock solution of well-characterized and *completely formed* Rh(0) nanoclusters synthesized under our standard conditions.[7] In each experiment, an aliquot of soluble Rh(0) nanoclusters was added to the reaction solution and a hydrogenation reaction was carried out as described in the Experimental Section. Once the initial catalytic activity of the unpoisoned Rh(0) nanoclusters was measured ($\{-dH_2/dt\}_i = 31 \pm 6$ psig/h), separate reaction solutions were prepared and then preselected amounts of either a 2.77×10^{-6} M or a 11.1×10^{-6} M CS_2 solution were added under a constant flow of hydrogen. Figure 2 shows the plot of relative rate vs moles of CS_2/moles of *total* Rh by the polyoxoanion-stabilized Rh(0) nanoclusters.

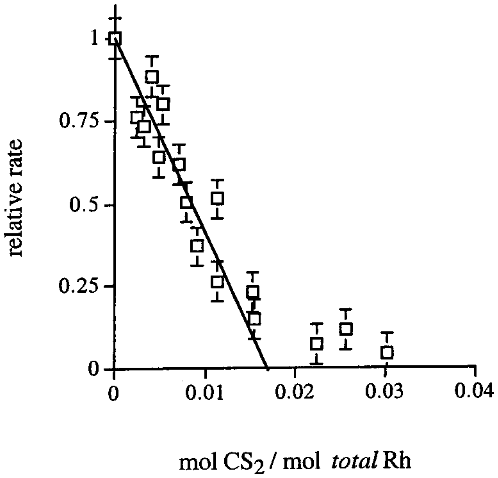

Figure 2. Plot of relative rate vs moles of CS_2/moles of *total* Rh for the hydrogenation of cyclohexene by the 40 ± 6 Å Rh(0) nanoclusters. Rates were determined by the initial-rate method from H_2 pressure vs time data taken over the course of 1 h (Figure G, Supporting Information); the $x_{\text{intercept}}$ is 0.018 ± 0.002 mol of CS_2/mol of *total* Rh. The experimentally nonzero rate past a CS_2/total Rh ratio of 0.018 probably indicates that the data in this figure actually defines a curve for reasons that are discussed in the text.

The $x_{\text{intercept}}$ was calculated from linear regression analysis of the linear portion of the experimental data and eq 2 ($y_{\text{intercept}} = 0.97 \pm 0.04$ and $m = 50 \pm 5$).[34] The $x_{\text{intercept}}$ is 0.018 ± 0.002 mol of CS_2/mol of *total* Rh, that is, *only half the value found for the heterogeneous 5% Rh/Al_2O_3 catalyst.* There is some apparent curvature in Figure 2 as evidenced by the nonzero rates seen past the intercept value. An analysis and discussion of this point is deferred until the Discussion section.

4. Additional Control Experiments. A. The Effect of Added Polyoxoanion. These experiments were designed to test whether or not the presence of the nanocluster-stabilizing $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion (i) could influence the poisoning efficiency of CS_2 as indicated by a change in value of the $x_{\text{intercept}}$ of the poisoning plot, or (ii) could affect the shape of the otherwise linear poison plot. The 5% Rh/Al_2O_3 catalyst with its otherwise straight-line poison plot (Figure 1) was the obvious best initial candidate for conducting these control experiments.

Experiments identical to those in Figure 1 were carried out except that 1.0 equiv of $(Bu_4N)_9[P_2W_{15}Nb_3O_{62}]$ was added per 1.0 equiv of *total* Rh(0) present in the 5% Rh/Al_2O_3 catalyst. Fourteen independent cyclohexene hydrogenation reactions were performed, with varying amounts of CS_2 (Supporting Information, Figure H). Figure 3 shows a plot of relative rate vs moles of CS_2/moles of *total* Rh. Extrapolation to the x-axis results in an intercept of 0.038 ± 0.005 ($y_{\text{intercept}} = 0.941$ and $m = 26.0$), a value within experimental error of that obtained from the experiment without added $[P_2W_{15}Nb_3O_{62}]^{9-}$, 0.035 ± 0.004. The key results from this control are that adding 1.0 equiv of the polyoxoanion (i) appears not to affect the number of *poisonable* active sites on the 5% Rh/Al_2O_3 catalyst surface but (ii) does slow the catalytic rate *by an order of magnitude* (from $\{-dH_2/dt\}_i = 52 \pm 3$ psig/h to 5 ± 2 psig/h) and (iii) does produce a nonzero rate past the intercept. The similarity in the $x_{\text{intercept}}$ values of the two experiments (with and without $[P_2W_{15}Nb_3O_{62}]^{9-}$) strongly suggests that there is no detectable interaction between the poison and the added

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(33) In the literature[12,18a] the equation used is $\nu/\nu_o = 1 - \alpha\theta$, which is equivalent to our eq 1 for $y = \nu/\nu_o$, $y_{\text{intercept}} = 1$, and $-mx = -\alpha\theta$.

(34) It is common practice in the poisoning literature to extend the linear portion of the poison plot to the x-axis. (See refs 12, 16, and 22b).

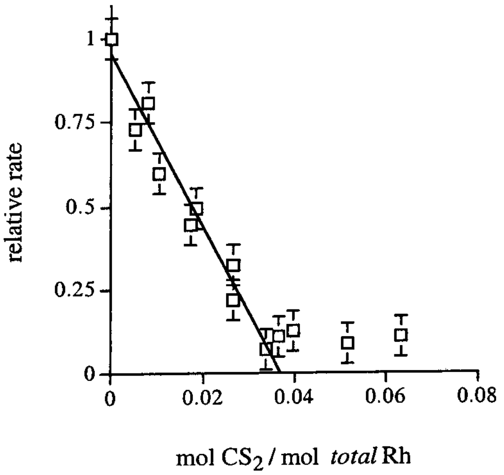

Figure 3. Plot of relative rate vs moles of CS_2/moles of *total* Rh for cyclohexene hydrogenation catalyzed by 5% Rh/Al_2O_3 with 1 equiv of $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ polyoxoanion per *total* Rh. Rates were determined by the initial-rate method from H_2 pressure vs time data taken over the course of 1 h (Figure H, Supporting Information); the $x_{\text{intercept}}$ is 0.038 ± 0.005 mol of CS_2/mol of *total* Rh. The experimentally nonzero rate past a CS_2/total Rh ratio of 0.038 probably indicates that the data in this figure actually defines a curve for reasons that are discussed in the text. Note also that the error bars on the points past 0.04 mol of CS_2/mol of *total* Rh are believed to be the maximum error bars; that is, a nonzero rate is in fact observed experimentally in the five rightmost points.

$[P_2W_{15}Nb_3O_{62}]^{9-}$. The slowed rate confirms the expected coordination of the polyoxoanion to the same surface sites that are responsible for catalysis. Noteworthy here is the now overwhelming evidence, in the case of the Rh(0) nanoclusters and as fortified by this CS_2 poisoning data, *that the polyoxoanion is coordinated to the nanoclusters' surface.*[35]

B. Control Experiments That Test for the Reversibility[36] of CS_2 Poisoning of 5% Rh/Al_2O_3 and Polyoxoanion-Stabilized Rh(0) Nanoclusters under the Reaction Conditions. It is important to be certain whether or not the poisoning by the volatile CS_2 (bp = 46 °C) is "reversible" under our conditions of a pressurized, *closed* Fischer−Porter bottle system. Hence, a control experiment was designed to test this possibility. Specifically, a cyclohexene hydrogenation experiment with 5% Rh/Al_2O_3 was initiated, after 1 h a single aliquot of CS_2 was added, and then the catalytic cyclohexene hydrogenation activity was monitored at 1.5 h intervals by the initial-rate method. A plot of the relative rate vs time, for two separate concentrations of CS_2, is shown in Figure 4. This plot shows that the catalytic activity of 5% Rh/Al_2O_3 is decreased to 28% and 2.5% of the initial catalytic activity with the addition of 6.6×10^{-9} and 1.7×10^{-8} mol of CS_2, respectively. Over the subsequent 6 h period, the catalytic activity of the 5% Rh/Al_2O_3 *remained at the depressed value without any restoration of activity,* as expected for irreversible binding of CS_2 to the catalyst surface.[37] Similar reversibility experiments were carried out with the soluble Rh(0) nanoclusters, and they, too, are consistent with irreversible binding of CS_2 to the surface under the closed reaction system conditions (see Figure I in the Supporting Information).

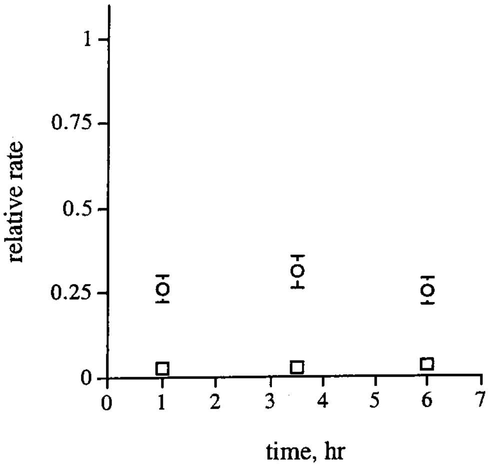

Figure 4. Plot of the relative rate vs time for cyclohexene hydrogenation catalyzed by 5% Rh/Al_2O_3 in the presence of two different amounts of CS_2: (topmost points) 6.6×10^{-9} mol of CS_2; (bottom-most points) 1.7×10^{-8} mol of CS_2. Rates were determined by the initial-rate method from H_2 pressure data collected over the course of 1 h. After each data point the Fischer−Porter bottle was repressurized to 40 ± 1 psig of H_2.

An interesting feature of Figure I is the reproducible decrease in the relative rate vs time after a single addition of CS_2, but repressurization at each point to 40 psig of H_2 (see Figure I). A slow, interesting, but presently poorly understood reaction between CS_2 and additional surface Rh (i.e., resulting in a greater number of Rh atoms being poisoned per CS_2) is implied or, perhaps, CS_2-induced agglomeration of the Rh nanoclusters.

However, on reflection we judged it important to conduct a more rigorous test for the reversibility of CS_2 binding by carrying out an experiment in an *open* system, where any unbound, volatile CS_2 could escape, thereby driving any putative CS_2 loss reaction to completion. An experiment was set up similarly to the conditions given above and using the 5% Rh/Al_2O_3 catalyst, except that the reaction solution was now subjected to a series of H_2 purge and vent cycles. As Figure 5 shows, there is still no recovery of catalytic activity, even after 5 h. This control experiment demonstrates that the various H_2 purging and repressurization procedures carried out throughout this study do not affect the concentration of CS_2 on the 5% Rh/Al_2O_3 catalyst surface despite the volatility of CS_2. In summary, the above experiments demonstrate the irreversibility of CS_2 binding to the 5% Rh/Al_2O_3 and to the Rh(0) nanocluster catalyst surfaces under open, as well as closed, reaction vessel and the other stated conditions.

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(35) Evidence that $P_2W_{15}Nb_3O_{62}^{9-}$ is bound to the surface of the metal(0) nanoclusters is provided by (i) electrophoresis (the otherwise neutral M(0) nanoclusters behave as anions; hence the only anion present, the polyoxoanion, must be bound to the nanoclusters) and (ii) the decrease in the catalytic activity as increasing amounts of polyoxoanion are added—compelling electrophoresis plus kinetic evidence that the polyoxoanion binds at the same M(0) surface site where catalysis occurs.[4a]

(36) These experiments also serve to characterize the catalyst poison, CS_2, as either "temporary" or "permanent" according to definitions put forth by Butt,[13] who suggests that these assignments be made based on the "degree of reversibility" associated with the poison/catalyst surface interaction. Throughout the main text, the terms "reversible" and "irreversible" are used in preference to the less well defined "temporary" and "permanent".

(37) Hydrogenolysis of CS_2 on a 1.6% Ru/Al_2O_3 catalyst at 425−675 K gives CH_4 and other products; those conditions are, however, much more vigorous than those employed herein. Gupta, N. M.; Kamble, V. S.; Iyer, R. M. *J. Catal.* **1981**, *69*, 111−120.

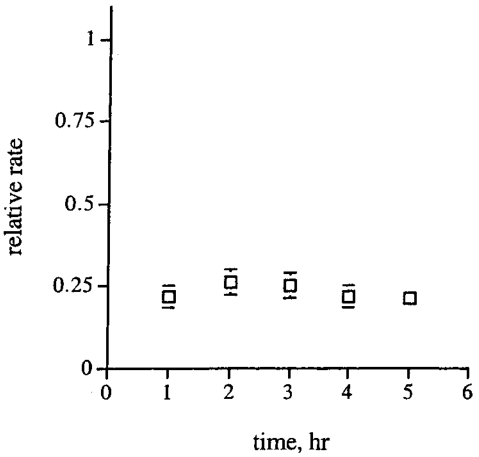

Figure 5. Plot of the relative rate vs time for cyclohexene hydrogenation catalyzed by 5% Rh/Al_2O_3 in the presence of 8.8×10^{-7} M CS_2. Rates were determined by the initial-rate method from H_2 pressure data collected over the course of 1 h. After each data collection period the Fischer−Porter bottle was purged several times and vented to the atmosphere before it was repressurized to 40 ± 1 psig of H_2.

Discussion

Prior to the present studies the following questions remained: what percentage of the total metal in the Rh(0) nanoclusters is actually catalytically active? How does this value compare to that for a prototype 5% Rh/Al_2O_3 heterogeneous catalyst selected to have at least average metal particles in the same size range? What are the per-metal-atom-based turnover frequencies (TOFs) for the two catalysts, and how do they compare? Is the common belief that nanoclusters are more active than their heterogeneous counterparts supported or refuted in a more rigorous, CS_2 poisoning based activity analysis? Overall, can poisoning methods such as the CS_2 method be used in nanocluster chemistry? The results of the present work answer each of these questions and lead to other, more general conclusions as detailed below.

1. Quantitative CS_2 Poisoning of 5% Rh/Al_2O_3 and Associated Control Experiments. The H_2 and CO chemisorption data on the 5% Rh/Al_2O_3 catalyst are in agreement; ca. 33% of the total Rh is present as *exposed* surface Rh atoms. Although chemisorption sites are not synonymous with catalytically active ones, the value of 33% represents the maximum number of active sites available on the 5% Rh/Al_2O_3 catalyst.[10] Key observations in Figure 1, plotting the relative rate vs moles of CS_2/moles of *total* Rh, are that (i) this plot is linear; (ii) the $x_{\text{intercept}}$ is 0.035 ± 0.004; and (iii) when combined with the 33% exposed Rh(0) value, one finds that 0.11 mol of CS_2/mol of *exposed* Rh metal completely deactivates the 5% Rh/Al_2O_3 catalyst. Moreover, this 0.11 value is in general agreement with values reported in the literature (i.e., where, for example, ca. 0.1 to ca. 0.60 equiv of CS_2 per exposed metal present are required to deactivate Pt/SiO_2, Pt/Al_2O_3, Pd/SiO_2, Pd/Al_2O_3, or Rh/SiO_2 olefin hydrogenation catalysts[10,14,15,18]). The exact structure(s) of CS_2 on any of these metal surfaces remains to be established, however.[38]

Table 1. Comparison of the CS_2 Poisoning Results for the Heterogeneous 5% Rh/Al_2O_3 and the Soluble Rh(0) Nanoclusters

	5% Rh/Al_2O_3	Rh(0) nanoclusters
% Rh on the surface	33%[b]	28−34%[a]
moles of CS_2/moles of total Rh for >90% inactivity	0.035 ± 0.004	0.018 ± 0.002
moles of CS_2/moles of exposed Rh for >90% inactivity	0.11 ± 0.01	0.06 ± 0.01

[a] Percentage estimated from "naked" magic number nanoclusters of $Rh(0)_{\sim 1400}$ to $Rh(0)_{\sim 4000}$ which correspond to the experimentally determined nanocluster size of 40 ± 6 Å.[6,8] [b] Determined by H_2 and CO chemisorption.

The apparent curvature in the plots induced by added polyoxoanion, Figure 3 (and a similar curvature in Figure 2 for the polyoxoanion-stabilized nanoclusters), can be explained in at least a couple of ways: competitive binding to the same active site by the polyoxoanion and CS_2 would affect (decrease) the apparent binding constant of the CS_2 (since the CS_2 addition reaction would now involve a polyoxoanion displacement in an equilibrium process), or it is conceivable that the polyoxoanion itself has a low level of hydrogenation activity that is not poisonable by CS_2. (The possibility that the polyoxoanion binds at a second type of site that remains active and thus unpoisonable by CS_2 is ruled out by the fact that the intercept did not change.) A control experiment was done which establishes that the polyoxoanion itself has negligible catalytic activity under the reaction conditions (see the Experimental Section). Hence, it would appear that the competition between the polyoxoanion and CS_2 for coordination to the active site is the source of the apparent curvature in Figures 2 and 3. Regardless of the exact explanation for the apparent curvature, the important fact is that the intercept is unchanged in Figure 1 vs Figure 3. This, in turn, provides confidence in the intercept value in both the absence, and presence, of nanocluster-stabilizing anions such as polyoxoanions.

2. Quantitative CS_2 Poisoning of Polyoxoanion-Stabilized Rh(0) Nanoclusters. The relative rate vs moles of CS_2/moles of *total* Rh(0) plot in Figure 2 for the polyoxoanion-stabilized Rh(0) nanoclusters and its comparison to the values for 5% Rh/Al_2O_3 are summarized in Table 1 and provide at least five important findings. First, it demonstrates that CS_2 can act as a powerful catalyst poison for soluble, solution-phase nanoclusters. This is proof-of-concept that CS_2, a well-known poison of traditional heterogeneous catalysts,[14,15,24] can also act as a poison of at least the present, solution-phase, Rh(0) nanoclusters. Second, only a small amount of CS_2 (0.018 equiv, 1−3% vs the *total* Rh present) destroys >90% of the catalytic activity of the Rh(0) nanoclusters. Third, one can estimate[39] that only 5−6% of the *exposed* Rh(0) in the nanoclusters is active for cyclohexene hydrogenation at the specified conditions, Table 1. This is a factor of ca. 2-fold *less* than the 10−12% of *exposed* Rh(0) atoms that are active in the 5% Rh/Al_2O_3 catalyst (3−4% of the

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(38) For two systems, CS_2/Cu(111)[38a] and CS_2/Cu(100),[38b] the CS_2 molecule was shown to lie nearly flat on the surface, thus interacting with more than one metal atom. (a) Yagi, S.; Yokoyama, T.; Kitajima, Y.; Takata, Y.; Kanazawa, T.; Imanishi, A.; Ohta, T. *Surf. Sci.* **1994**, *311*, 172−180. (b) Yagi, S.; Takenaka, S.; Yokoyama, T.; Kitajima, T.; Imanishi, A.; Ohta, T. *Surf. Sci.* **1995**, *325*, 68−74

Table 2. Summary of the Catalytic Activities of the Heterogeneous 5% Rh/Al$_2$O$_3$ and the Soluble Rh(0) Nanoclusters

	5% Rh/Al$_2$O$_3$	Rh(0) nanoclusters
absolute rate^a	26 ± 2 psig/h	31 ± 6 psig/h
TOF (based on total Rh)	28 800 h^{-1}	34 300 h^{-1}
TOF (corrected for exposed Rh)	87 100 h^{-1}	110 600 h^{-1}
TOF (corrected for active Rh atoms determined by CS$_2$ poisoning and using, for the sake of illustration, a 1/5 CS$_2$/Rh stoichiometry)^b	164 300 h^{-1}	380 900 h^{-1}
rel TOF	1	2.3
rel TOF if the effect of 1.0 equiv of [P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{9-}$ is included as an upper limit estimate	1	23
TTOs^c	350 000^c	193 000^c
TTOs^c (corrected for active Rh atoms determined by CS$_2$ poisoning and using an estimated 1/5 CS$_2$/Rh stoichiometry)^b	2 000 000^{c,d}	2 142 000^{c,e}

[a] Values based on 3.20 × 10^{-7} mol of *total* Rh(0). [b] See the text for a discussion of the single-crystal literature leading to this working estimate of a 1/5 CS$_2$/Rh stoichiometry that is used in the above table for the sake of illustration. [c] Data taken from ref 8. [d] Correction factor: 1/(0.035*X*), where *X* is estimated as 5. [e] Correction factor: 1/(0.018*X*), where *X* is estimated as 5. Note that the Rh(0) nanoclusters produced under the conditions of this TTO lifetime experiment average 26 Å, not 40 Å, as detailed in ref 8 and discussed further in footnote 47.

total Rh present). The 2-fold lower number of active Rh(0) sites in the nanocluster is most readily explained by the polyoxoanion binding to the nanoclusters' surface, thereby stabilizing it toward agglomeration[4,5] and concomitantly inhibiting the nanoclusters' catalytic activity. Stabilization of such nanoclusters is, therefore, shown to be at the expense of catalytic activity, as expected. Bradley has reached the same conclusion for polymer-stabilized nanocolloids.[40]

Fourth, the small 0.018 CS$_2$/Rh(0) ratio in the nanoclusters cannot be explained by a homogeneous, single-metal-site, Rh$_1$ catalyst, as such a catalyst would be expected to require $\geq$1 equiv of CS$_2$ per mol of *total* Rh to be poisoned fully. This is a nontrivial finding in its own right since it is additional evidence[8] that Rh(0) nanoclusters are the true catalysts in this system—a CS$_2$/Rh(0) ratio that is $\ll$1 requires that much of the Rh(0) be inaccessible, which in turn requires a geometry where a significant fraction of the Rh(0) is on the "inside" of the resultant (nanocluster) structure. And, finally, these values are in the general range of the only other poisoning values available for nanoclusters in the literature, specifically, Moiseev and co-workers' report of complete deactivation at CS$_2$/total Pd ratios of 0.091 and 0.027 for Pd$_{\sim 560}$phen$_{\sim 60}$(PF$_6$)$_{\sim 60}$O$_{\sim 60}$ catalyzed ethylene and propylene oxidation, respectively.[16] Note that the ~3-fold smaller ratio when the larger propylene (vs the smaller ethylene) molecule is present appears to reflect the crowding at the Pd nanoclusters' surface.[16]

Interestingly, the polyoxoanion-stabilized Rh(0) nanoclusters are ca. 20-fold longer-lived catalysts in comparison to the Pd$_{\sim 560}$ nanoclusters (see footnote 15 elsewhere[8]), even though the former *appear* to have less catalytically active metal available. Factors contributing to this apparently different activity likely include the differences between the two types of reactions catalyzed (oxidations vs reductions), the different metals, Rh vs Pd, and the possibility that the poisoning data reported for the Pd$_{\sim 560}$ system may well represent an upper limit (i.e., if the S-based poisons employed are oxidized under the (oxidative) reaction conditions employed elsewhere).[16]

3. A Comparison of the Catalytic Activities for the Rh(0) Nanoclusters and the 5% Rh/Al$_2$O$_3$ Heterogeneous Catalyst. The CS$_2$ poisoning data allow an important, previously unavailable comparison of the initial rates of cyclohexene hydrogenation for the Rh(0) nanocluster vs the heterogeneous catalyst, Table 2, and assuming that the CS$_2$/Rh stoichiometry ratio is the same for the two catalysts: the inherent activity of the Rh(0) nanoclusters is *an apparent ca. 2.3-fold higher per active site* than the oxide-supported Rh catalyst.

Given that the 5% Rh/Al$_2$O$_3$ catalyst was likely synthesized and activated at high temperatures, yet the nanoclusters are synthesized at lower temperatures (22 °C) under kinetic control conditions,[4b,c,41] it seems highly likely that the nanocluster surface is much rougher with *multiple types of active sites differing, ultimately, in their number of nearest Rh atoms and, therefore, their coordination number*. Other factors that may account for the differing activity is the presence in the relatively "dirty" 5% Rh/Al$_2$O$_3$ catalyst of Cl$^-$, O$_2^-$, OH$^-$, H$_2$O (poisons deliberately avoided in this and all our other syntheses of polyoxoanion-stabilized nanocluster catalysts) or other common (and typically ill-defined) surface impurities in heterogeneous catalysts.[42] Effects due to the oxide support are also possible.[43] Finally, the more different the Rh(0) nanocluster and 5% Rh/Al$_2$O$_3$ catalysts (rough vs smoother, or other differences), the more likely the CS$_2$/Rh stoichiometry ratio is at least somewhat different for the two catalysts and, therefore, part of the *apparent* ca. 2.3-fold higher rate per active site for the Rh(0) nanoclusters.

Noteworthy here is that the 2.3-fold rate difference does not include the effect of the [P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{9-}$ on the nanocluster catalyst's surface. Given our demonstration that the initial rate of the 5% Rh/Al$_2$O$_3$ catalysts is reduced by an order of magnitude by 1.0 equiv of added [P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{9-}$,

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(39) This 5−6% estimate is readily derived using the 0.018 value, a 1/1 CS$_2$/Rh(0) stoichiometry, and the 40 ± 6 Å size of the nanoclusters to calculate[9] that between 28% and 34% of the total Rh(0) atoms in the nanocluster are *surface* Rh(0) atoms.

(40) de Caro, D.; Bradley, J. S. *New J. Chem.* **1998**, *22*, 1267−1273.

(41) Widegren, J. A.; Aiken, J. D., III; Özkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312−324.

(42) (a) Jacobs, P. W.; Somorjai, G. A. *J. Mol. Catal. A: Chem.* **1998**, *131*, 5−18. Köhler, J.; Bradley, J. S. *Catal. Lett.* **1997**, *45*, 203−208. (b) Bond, G. C. *Acc. Chem. Res.* **1993**, *26*, 490−495.

(43) Frety, R.; DaSilva, P. N.; Guenin, M. *Catal. Lett.* **1989**, *3*, 9−16.

the preliminary implication is that the intrinsic activity of hypothetical "naked" Rh(0) nanoclusters is, then, between 2.3 *and 23 times* that of the heterogeneous catalyst on a per-active-metal-atom basis. The above results provide for the first time more reliable, poison-study determined, rates of metal-particle heterogeneous and soluble nanocluster catalysts for a direct comparison.[44]

4. The Exact CS_2/Rh(0) Stoichiometry Ratio: A Target for Future Research. Nothing to this point has required knowledge of the exact CS_2 to Rh(0) stoichiometry required to poison a single active site; to this point the only assumption has been that the Rh(0) nanocluster and 5% Rh/Al_2O_3 catalysts have a similar CS_2/Rh poisoning ratio—although as noted above, possible different roughness or other differences in the surfaces of the two catalysts will likely mitigate against even this assumption being exactly true.

To proceed further, for example to obtain the absolute number of active sites, one needs an experimental measurement of the exact CS_2/Rh poisoning stoichiometry ratio for both catalysts and under the exact reaction conditions. Such numbers are presently unavailable; indeed, even the required methods to measure such stoichiometries for nanoclusters in solution are not yet available. This lack of exact CS_2/Rh poisoning stoichiometry ratios has clearly been the Achilles heel of the catalyst poisoning method, at least for determining the absolute number of metal active sites and the associated, *absolute* TOF (turnover frequency), and at least until the single-crystal data cited below. This Achilles heel is, however, not unique to the nanocluster area; rather, all of the catalyst poisoning literature, as well as all of the H_2 or CO chemisorption literature (see, for example, footnote 30), suffers from the issue of "what is the poison/metal stoichiometry ratio, especially under the reaction conditions?"

However, the prior heterogeneous catalysis literature, especially the single-crystal literature, as well as the well-defined nature and relatively narrow size distribution of nanoclusters (±15%; so-called near-monodisperse[2,3]) offers some help here:[45] ratios from ca. 1/1.5 to 1/10 appear to be most common. Also relevant to this discussion is that of the seven available structures of small-molecule organometallic complexes containing CS_2, all but two of them have a CS_2/metal ratio of 1/2, one structure having a 1/1 and one a 1/3 CS_2/metal ratio (see structures XXV−XXXI elsewhere[46]). Turkevich's CS_2 poisoning studies of colloidal Pt/Al_2O_3 or SiO_2 catalysts are also noteworthy in that he found CS_2/metal ratios that tended to fall in two groups, 1/2 or 1/(4−8), for reasons that were not stated.[10]

For the Rh(0) nanoclusters, we know, first, that the CS_2/*total* Rh ratio is the experimentally determined 0.018 value. We also know that, for the 40 ± 6 Å (i.e., 34−46 Å) Rh nanoclusters of, therefore, ca. 7 shell ($n = 7$)[9] $Rh_{\sim 1500}$ to 9 shell ($n = 9$)[9] $Rh_{\sim 3700}$ total atoms, ca. 34% and 28%, respectively, of the metal atoms are on the surface, about 31% on average (and using the $n = 6$ and 8 shell nanoclusters to get the number of metal atoms *underneath* the surface of the idealized $n = 7$, $Rh_{\sim 1415}$, and $n = 9$, $Rh_{\sim 2869}$, nanoclusters).[9] The *maximum* CS_2/Rh ratio for the nanoclusters is, therefore, 1.8/31 or *1/17*, a value that is within the 1/1.5 to 1/20 limits seen from the single-crystal studies. It seems likely that the real ratio is one-third to one-half of this value, perhaps 1/5 to 1/8, based on the single-crystal literature cited above. We have gone ahead and used a value of 1/5 for the purposes of illustration in some sample calculations made in Table 2. As shown in Table 2, the true TOF and TTO values for the Rh(0) nanoclusters are a factor of $1/(0.018X)$ which equals $55/X$ higher than the apparent, lower limit TOF of 34 300 h^{-1}, and (already record[32]) TTO of 193 000, where X is the CS_2/Rh stoichiometry ratio. If one takes a value of X of ca. 5 as a reasonable guesstimate based on the single-crystal data cited earlier and *for the sake of illustration* as done in Table 2, then the *per true active site* TOF increases to 380 900 h^{-1} and the TTO value increases to an impressive 2 142 000 total turnovers of cyclohexene hydrogenation per true active site![47] Noteworthy is that, if the same X value holds true for both the nanocluster and 5% Rh/Al_2O_3 catalyst, then the Rh(0) nanocluster's estimated 2 142 000 TTOs is as good as if not slightly better than that of the 5% Rh/Al_2O_3 catalyst, 2 000 000 TTOs, Table 2. These sample calculations make apparent that an important research objective which remains is to measure experimentally the poisoning stoichiometry ratio in solution for this and at least several other nanocluster systems as well as their heterogeneous catalyst counterparts.

Summary and Conclusions

In summary, the CS_2 poisoning experiments on polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters and on a commercial 5% Rh/Al_2O_3 catalyst, plus a variety of control experiments, have led to the following conclusions and insights, each of which was previously unavailable:

(i) The prototype CS_2 poisoning method has been developed herein for, and shown to work with, Rh(0) nanoclusters (and by implication other transition-metal nanoclusters); the method is found to work as well with the nanoclusters as it

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(44) It would be of interest to compare the absolute rates per metal atom of *oxide-supported* nanocluster catalysts to the two catalysts studied herein and under conditions identical to those used herein. Such studies may prove helpful en route to achieving the heterogeneous catalysis "Holy Grail" of single-site heterogeneous catalysts; see the Vision 2020 Catalysis Report: www.ccrhq.org/vision/index/roadmaps/catrep.html.

(45) Reported poison/metal-atom stoichiometries range from 1/1.5, for S deactivation of H_2/D_2 exchange to 2H−D on Pt(111) at 170 °C,[20] to 1/4, for S on Ni(100) (for blocking H_2 or CO adsorption at 300 K);[22] and finally from 1/10 to 1/20 for S inhibition of methane synthesis from 120 Torr of 4/1 H_2/CO at 600 K.[20,22a] The poison-to-metal ratios obviously can vary widely for different metals and metal surfaces and as a function of the poison and reaction being examined, and perhaps also the temperature. Long-range electronic effects due to the poison are believed to be operative as well, effects that result in ratios <1.[17a,20−22]

(46) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37−114.

(47) Note that the Rh(0) nanoclusters produced under the conditions of the TTO lifetime experiment average 26 Å, not 40 Å, as detailed in ref 8. Hence, they have somewhat more surface Rh per total Rh and will, therefore, likely require more poison than the 0.018 value; therefore, the correction factor ($1/0.018X$) will be lower. Restated, the 2 142 000 estimate is expected to be an upper limit for the 26 Å nanoclusters.

does in control studies using a traditional 5% Rh/Al_2O_3 heterogeneous catalyst, at least under the reductive reaction conditions examined.

(ii) A number of useful controls to use the method properly were pointed out and performed, controls to avoid H_2 gas-to-solution mass-transfer limitations, controls to be sure the volatile CS_2 solution is freshly made and otherwise is not lost during the poisoning reactions, controls to be sure that the CS_2 poisoning is not reversible under the (mild) reaction conditions; controls to be sure the nanoclusters fully evolve (using the valuable cyclooctane evolution handle), and controls using a direct ^{1}H NMR method to verify the (preferred) initial rate method used.

(iii) In comparison to the total amount of metal present, the percentage of Rh(0) on the surface of the nanocluster is ~31% while the percentage of catalytically active Rh(0) (again, vs the total Rh present) is ~1.8%; the analogous values for the 5% Rh/Al_2O_3 catalyst are 33% and ~3.5%. Hence, the number of active sites is ca. 2-fold less in the nanocluster.

(iv) The similarity of the values is consistent with, and supportive of, the developing analogy of nanoclusters as "soluble analogs of heterogeneous catalysts." [2]

(v) The activity of the Rh(0) nanoclusters is at least 2.3 times greater than that of the 5% Rh/Al_2O_3 heterogeneous catalyst, based on the number of active sites determined by the CS_2 poisoning experiments;

(vi) Adding 1.0 equiv of $(Bu_4N)_9[P_2W_{15}Nb_3O_{62}]$/*total* Rh(0) to the 5% Rh/Al_2O_3 catalyst results in a 10-fold reduction in the heterogeneous catalyst's activity. This strongly suggests that the high stability and record catalytic lifetime of the polyoxonion-stabilized Rh(0) nanoclusters[8] is, however, achieved at the price of a similar, ~10-fold reduction of their catalytic activity.

(vii) The implication is then, however, that if the Rh(0) nanoclusters could be prepared in forms having a more "naked surface", their activity would be up to ca. 23-fold greater than that of the 5% Rh/Al_2O_3 catalyst. The use of clean-surface nanoclusters, that is, ones made under conditions that avoid O_2, X^- (halide), and other such ligands, to make supported catalysts is, therefore, indicated to be a worthwhile goal. A number of efforts in this direction have already been reported (see the references and discussion available elsewhere[3]).

(viii) Another implication of these results is that the true TOF and TTO values for the Rh(0) nanoclusters are a factor of $55/X$ higher than the apparent (lower limit) TOF of 34 300 h^{-1} (Table 2), and (already record[32]) TTO of 193 000, where X is the CS_2/Rh stoichiometry ratio. Using a value of X of ca. 5 for the sake of illustration, the per true active site TOF increases to 380 900 h^{-1} and the TTO value increases to 2 142 000 total turnovers of cyclohexene hydrogenation per true active site,[47] the latter being as large as if not better than the value obtained for the 5% Rh/Al_2O_3 catalyst, Table 2. These values illustrate the use and significance of poisoning data such as that obtained herein, especially if the exact CS_2/Rh stoichiometry ratio, X, can be obtained in future work.

(ix) An important research goal is to develop the methods, and then to use them to measure, the true poison/metal stoichiometry ratios in solution and under the catalytic reaction conditions. The identification of the exact structure(s) of CS_2[46] (and other ligands[48]) attached to the nanocluster surfaces is another unattained research goal.[49] Single-crystal studies looking at the same metals, and different crystal faces of those metals, with CS_2 would also be quite valuable.

(x) The CS_2 or other applicable poisoning methods should be used in conjunction with recently developed chemisorption methods for nanoclusters in solution,[11] to provide the best available estimates of the percentage of active metal and the per-active-metal-atom TOF. Nanocluster catalysis scientists should follow the lead of Boudart's pioneering work,[26] and use this crucial indicator of metal-particle catalysis performance, the TOF.

Overall, there is every reason to believe that CS_2 and other poisoning studies will become at least as important in nanocluster catalysis as they are in traditional heterogeneous catalysis.[10,12−24] The present studies are, however, just the start of the needed nanocluster poisoning studies.[50]

Experimental Section

1. Materials and Instrumentation. Unless otherwise specified, all reaction solutions were prepared under oxygen- and moisture-free conditions in a Vacuum Atmospheres drybox (<5 ppm O_2 as continuously monitored by a Vacuum Atmospheres O_2 monitor.) Cyclohexene (Aldrich 99% with stabilizer) was distilled from sodium under argon and stored in the drybox (purity >99% by GC). Acetone (Burdick and Jackson, 0.26% H_2O) was purged with argon for 20 min to remove any dissolved O_2 before it was transferred to the drybox. Carbon disulfide (Aldrich 99.9+%) was used as received; 5% Rh/Al_2O_3 was obtained from Strem Chemicals and was preactivated under H_2 by the manufacturer. The percent of exposed surface metal (dispersion) of the 5% Rh/Al_2O_3 sample was obtained by H_2 and CO chemisorption performed by Micromeritics (Norcross, GA) using a Micromeritics 2010C instrument with the usual assumptions of 2/1 (H_2/Rh) and 1/1 (CO/Rh) stoichiometries.[11a] The $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ polyoxoanion used in the synthesis of **1** and in some of the H_2 uptake experiments was synthesized according to our most recent procedure including its crucial improvements in the synthesis of the $P_2W_{15}O_{56}{}^{12-}$

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(48) A hydride species has been detected atop nanoclusters, but this species has not been shown to be a kinetically competent reaction intermediate. (a) See ref 16b above. (b) Kozitsyna, N. Y.; Vargaftik, M. N.; Moiseev, I. I. *J. Organomet. Chem.* **2000**, *593−594*, 274−291 and references therein.

(49) One perceived additional significance of nanocluster catalysis derives from the possibility of studying surface intermediates atop soluble nanoclusters and using the powerful array of solution spectroscopic methods that are available. Such studies hold promise of advancing the knowledge of the intimate mechanisms of metal particle catalysis, historically a thorn in the side of progress in heterogeneous catalysis.[2,42b] Such solution spectroscopic studies of nanoclusers derivatized with L $= CS_2$, olefin, H−, R−, RC(O)−, $R_2C=$, RC−, and other interesting ligands remain virtually unexplored, however, so this is another important goal for future studies in nanocluster catalytic science.

(50) For example, needed poisoning studies with nanoclusters include work comparing other poisons, as a function of different size reactants (smaller to larger olefins,[12,16] for example), for different metals, and poisoning studies in conjunction with spectroscopic studies (e.g., IR studies looking, for example, at the expected effects of CS_2 on CO mobility, the expected stronger metal−S bonds moving the CO into weaker adsorption sites as has been seen for heterogeneous catalysts[19]).

precursor.[51d] The purity of the resultant $[P_2W_{15}Nb_3O_{62}]^{9-}$ was >90% by ^{31}P NMR.[51] The precatalyst, $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]$, **1**, was prepared as previously described; its purity was confirmed by ^{31}P NMR and compared to the published spectrum (note that the downfield peak is reproducibly less intense than the upfield one).[7]

Nuclear magnetic resonance (NMR) spectra were obtained in either CD_3CN or CD_2Cl_2 in 5.0 mm o.d. NMR tubes from either Spectra Tech or Wilmad. Phosphorus (^{31}P) NMR spectra (121.5 MHz) were recorded on a Varian Inova 300 spectrometer at 21 °C and referenced to 85% H_3PO_4 (0 ppm) by either the substitution method or an internal capillary tube containing 85% H_3PO_4. Proton (^1H) NMR were obtained on the same instrument in CD_2Cl_2 and referenced to the residual solvent impurity.

Kinetic data (H_2 pressure vs time) was measured in 1.0 min intervals with an Omega model PX621 pressure transducer attached to a PC via an Omega WB35 A/D converter.[5,41] LabVIEW (version 2.5.1) software was used to collect the pressure vs time data, which was stored as a data file and exported to MicroCal Origin 5.0 for analysis.

2. General Procedure for Catalyst Poisoning Experiments. The Initial-Rate Method. All catalyst activity measurements were preformed on the previously described,[5] custom-built pressurized hydrogenation apparatus consisting of a pressurized Fischer−Porter bottle attached via Swagelock quick-connects to both a hydrogen supply (passed through water- and oxygen-scavengers) and to a pressure transducer. Unless otherwise stated, all reactions were carried out in the following manner and are based on our previously established reaction conditions for catalyst lifetime experiments:[6] in a drybox, the catalyst or precatalyst material was weighed into a disposable 2 dram glass vial. The material was then dissolved in acetone, and cyclohexene was added (both added by gastight syringe). The solution was mixed with a disposable polyethylene pipet and then transferred into a new 22 × 175 mm culture tube containing a new $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. (The use of a new culture tube and a new stir bar are precautions that we have long employed[5] to avoid heterogeneous nucleation of the nanocluster formation reaction.[4b]) The culture tube was then placed inside the Fischer−Porter bottle, sealed, brought from the drybox, placed in a constant temperature circulating water bath thermostated at 22.0 ± 0.1 °C, and attached to the hydrogenation apparatus via the quick-connects. Stirring was started (at >600 rpm), and the Fischer−Porter bottle was then purged 13 times with 40 psig of H_2 (15 s/purge). The reaction vessel was then pressurized to 40 ± 1 psig of H_2, and $t = 0$ was noted.

3. Data Treatment. The Initial-Rate Method. Initial rates, ($\{-dH_2/dt\}_i$, expressed in psig/h) were calculated from the pressure vs time data using the initial-rate method described elsewhere.[52] Briefly, the data were fitted to a polynomial expression using MicroCal Origin 5.0, Figures B, G, and H of the Supporting Information. At $t = 0$, $\{-dH_2/dt\}_i$ is the first-order coefficient of the polynomial fit and reproduced below for the function *f* of *t*, *f*(*t*).

$$f(t) = C_1 + C_2t + C_3t^2 + C_4t^3 \ldots$$

$$df/dt = C_2 + 2C_3t + 3C_4t^2 \ldots$$

At $t = 0$, $df/dt = C_2$, and since $\{-dH_2/dt\}_i = df/dt$ it follows that

$$\{-dH_2/dt\}_i = C_2$$

The initial rates determined in this manner were, for all experiments, within 3−5% of initial rates calculated from fitting the first 25% of the data to a straight line. Although both methods give similar values, those obtained from the more rigorous second-order polynomial fits are reported.

4. Quantitative CS_2 Poisoning Experiments of Hydrogenation Catalysts. A. Poisoning of 5% Rh/Al_2O_3. All the experiments were carried out in a similar manner: in a drybox, 2.5 mL of acetone and 2.5 mL of cyclohexene were added, using separate 5 mL gastight syringes, to a 2 dram vial containing 5% Rh/Al_2O_3 (1.3−1.4 mg). This solution was thoroughly mixed with a pipet and transferred to a new 22 × 175 mm culture tube containing a new $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was then placed inside the Fischer−Porter bottle, sealed, brought from the drybox, placed in a constant temperature water circulation bath thermostated at 22.0 ± 0.1 °C, and attached to the hydrogenation apparatus via the quick-connects. Stirring (>600 rpm) was started, and the Fischer−Porter bottle was purged 13 times with 40 ± 1 psig of H_2 (15 s/purge). After the thirteenth purge the ball valve of the Fischer−Porter bottle was left open and an aliquot (0.100−0.500 mL) of either a 3.32×10^{-5} M or a 1.11×10^{-5} M, CS_2 stock solution (in acetone) was added using either a 1 mL or a 500 μL gastight syringe fitted with a 9 in. stainless steel needle. A control experiment with 1 day old CS_2/acetone solutions indicated that the poison solutions should be made fresh each day (see the Supporting Information, Figure D). After the addition of poison, the reaction vessel was purged twice more (15 s/purge) and stirred for an additional 2 min before the pressure was set to 40 ± 1 psig and $t = 0$ was set. Since CS_2 has a relatively low boiling point (46 °C), the Fischer−Porter bottle was purged only twice to minimize its volatilization from the reaction vessel.

Before the initial rates were calculated from the pressure vs time data, the data was corrected for the acetone vapor pressure that accumulates in the Fischer−Porter bottle over the course of the reaction.[41] This point-by-point correction was determined by setting up a reaction exactly as described above, but with the omission of catalyst. Pressure vs time data was then collected for 1 h. The correction for each point is simply the difference between the data in Supporting Information, Figure J, and the initial pressure. These values were then subtracted from each raw data point, resulting in the pressure change due solely to H_2 uptake.[41] Since this acetone vapor correction affects all the initial-rate data, this experiment was carried out three times to ensure that the correction values remained effectively constant over the course of the study; see the Supporting Information, Figure J.

Plots of the corrected H_2 pressure vs time, with the corresponding polynomial fits, are provided in Figure B of the Supporting Information. A plot of the relative initial rate vs moles of CS_2/moles of *total* Rh for 5% Rh/Al_2O_3 is shown in Figure 1.

In addition, a control experiment was performed in which the initial amount of cyclohexene was doubled (from 2.5 to 5.0 mL). The observed initial rate did not change within experimental error

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(51) (a) Weiner, H.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 5, 7905−7913. Note that this manuscript has two errors: p 7910, right-hand column, twelfth line, “84% excess” should read “2% excess”; p 7910, footnote 20, fourth line, “5%” should read “0.5 M.” (b) Finke, R. G.; Lyon, D. K.; Nomiya, K.; Weakley, T. J. *Acta Crystallogr., Sect. C* **1990**, *C46*, 1592−1596. (c) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692−1704. (d) In order to reproducibly obtain high-purity $[P_2W_{15}Nb_3O_{62}]^{9-}$, it is crucial to follow our recent improvements in the synthesis of its precursor $[P_2W_{15}O_{56}]^{12-}$: Hornstein, B. J.; Finke, R. G., submitted for publication (The Lacunary Polyoxoanion Synthon $P_2W_{15}O_{56}{}^{12-}$: An Investigation of the Key Variables in Its Synthesis Plus Multiple Control Reactions Leading to a Reliable Synthesis).

(52) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: New York, 1991.

($\{-dH_2/dt\}_i = 50 \pm 4$ psig/h for 2.5 mL of cyclohexene and ($\{-dH_2/dt\}_i = 50 \pm 5$ psig/h for 5.0 mL of cyclohexene), a result which requires that the hydrogenation reaction is zero order in cyclohexene under these conditions.

Similar poisoning results were obtained by an alternate method (described in detail in the Supporting Information, Figure K) in which the CS_2 solution was prepared in the drybox and added to the reaction solution which was also in the drybox and before it was exposed to hydrogen. Although the order of poison/olefin/H_2 addition was shown to be important in a recent hydrogenation study,[53] the agreement between the two procedures suggests that the order of addition is not a factor in the present case. Since the poison study results are independent of the order of addition, it is recommended that the catalyst poison be manipulated outside of the drybox in order to limit the exposure of the drybox catalyst to CS_2.

B. Poisoning of 5% Rh/Al_2O_3 in the Presence of [(*n*-C_4H_9)$_4$N]$_9$-[$P_2W_{15}Nb_3O_{62}$]. Fourteen additional, independent 5% Rh/Al_2O_3 poisoning experiments, with CS_2, were performed with a ratio of 1/1 [(*n*-C_4H_9)$_4$N]$_9$[$P_2W_{15}Nb_3O_{62}$]/*total* Rh. All experiments were carried out in a similar manner: in a drybox, 5% Rh/Al_2O_3 (1.3−1.4 mg) was added along with 2.40 mL of acetone and 2.50 mL of cyclohexene to a 2 dram vial. To this solution was added 0.100 mL of a 6.44×10^{-3} M [(*n*-C_4H_9)$_4$N]$_9$[$P_2W_{15}Nb_3O_{62}$] solution in acetone (1.0 ± 0.1 equiv per total Rh) using a 500 μL gastight syringe. The reaction solution was thoroughly mixed with a pipet and transferred to a new 22 × 175 mm culture tube containing a new $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was then placed in the Fischer−Porter bottle, sealed, brought out of the drybox, placed in a constant temperature circulation water bath thermostated at 22.0 ± 0.1 °C, and attached to the hydrogenation apparatus via the quick-connects. As described above in section 4.A, the reaction vessel was purged 13 times, an aliquot of carbon disulfide was added with either a 1 mL or a 500 μL gastight syringe, $t = 0$ was set, and pressure vs time data was collected. Before this data was fitted, it was also corrected for the acetone vapor pressure contribution to the total pressure measured by the transducer. Point-by-point correction values were determined from a control solution containing 2.4 mL of acetone, 2.5 mL of cyclohexene, and 0.100 mL of a 6.44×10^{-3} M [(*n*-C_4H_9)$_4$N]$_9$[$P_2W_{15}Nb_3O_{62}$] solution. These correction values were the same, within experimental error, as those without [(*n*-C_4H_9)$_4$N]$_9$[$P_2W_{15}Nb_3O_{62}$].

Plots of the corrected H_2 pressure vs time with the corresponding polynomial fits (see above), are provided in Figure H of the Supporting Information. A plot of the relative rate vs moles of CS_2/moles of Rh for 5% Rh/Al_2O_3 with added [(*n*-C_4H_9)$_4$N]$_9$[$P_2W_{15}Nb_3O_{62}$] (polyoxoanion/Rh = 1) is shown in Figure 3.

C. Poisoning of Polyoxoanion-Stabilized Rh(0) Nanoclusters. In order to begin with a well-characterized catalyst, a stock solution of Rh(0) nanoclusters was prepared from the precatalyst, [(*n*-C_4H_9)$_4$N]$_5$Na$_3$[(1,5-COD)Rh·$P_2W_{15}Nb_3O_{62}$], **1**, by the standard conditions as described elsewhere.[4,6] Briefly, 20 mg (3.58×10^{-6} mol) of precatalyst was dissolved in 2.50 mL of acetone in the drybox. To this was added 0.50 mL of cyclohexene with a 1 mL gastight syringe. This solution was thoroughly mixed with a pipet and transferred to a 22 × 175 mm culture tube containing a $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was then placed in the Fischer−Porter bottle, sealed, brought from the drybox, placed in a constant temperature circulation water bath thermostated at 22.0 ± 0.1 °C, and attached to the hydrogenation apparatus via the quick-connects. After 19 h (to ensure that the 40 ± 6 Å Rh(0) nanoclusters were completely evolved; this was proven by a cyclooctane evolution experiment, vide infra) the solution was taken back into the drybox and transferred to a clean vial.[6,54]

Since the completely formed nanoclusters were partially insoluble in the reaction solution of acetone/cyclohexene/cyclohexane, they were quantitatively transferred in the drybox to a 10 mL volumetric flask and diluted to the 10 mL mark with acetone. The resulting clear amber solution was sealed and stored in the drybox for up to 2 days, but not more, before its use in the poisoning experiments described below. (A control reaction with a 10 day old nanocluster solution, which was stored in a sealed vial in the drybox, gave an unpoisoned initial rate of 8.2 psig/h. This value is 22% of the rate obtained with freshly prepared Rh(0) nanoclusters, 37.1 psig/h.)

All poisoning experiments with the preformed Rh(0) nanoclusters were carried out in the same manner. To a 2 dram vial was added 0.86 mL of the Rh(0) nanocluster stock solution (3.72×10^{-4} M in *total* Rh(0)) described above, followed by 2.5 mL of acetone and 2.5 mL of cyclohexene added with separate 5 mL gastight syringes. The solution was mixed with a disposable pipet, transferred to a new culture tube, and placed in a Fischer−Porter bottle as described above. After the bottle was attached to the hydrogenation line, it was purged 13 times with H_2 (15 s/purge) and an aliquot of CS_2 solution in acetone (2.77×10^{-6} or 11.1×10^{-6} M) was added with a 9 in. needle through the ball valve of the Fischer−Porter bottle and under a continuous flow of hydrogen. The Fischer−Porter bottle was purged two more times (15 s/purge) and pressurized to 40 ± 1 psig, and the solution was stirred for an additional 2 min before $t = 0$ was set. Pressure vs time data was collected for 1 h, and the initial rates for each ratio of CS_2/*total* Rh(0) were calculated from the acetone vapor pressure corrected data, as described above. This experiment was repeated several times, and the data is shown as a plot of relative rate vs moles of CS_2/moles of *total* Rh(0) in Figure 2.

Similar to the heterogeneous catalyst, a control experiment was carried out with the soluble Rh(0) nanoclusters in which the initial amount of olefin present was doubled. This resulted in similar rates within experimental error ($\{-dH_2/dt\}_i = 19.6 \pm 0.5$ psig/h for 2.5 mL of cyclohexene and $\{-dH_2/dt\}_i = 20.0 \pm 0.2$ psig/h for 5.0 mL of cyclohexene), results which require that the initial rate be independent of cyclohexene concentration under these conditions.

5. Semiquantitative Catalyst Poisoning Experiments Using CS_2. ^{1}H NMR Method as a Control. Poisoning of 5% Rh/Al_2O_3. A catalyst lifetime experiment was started beginning with 5% Rh/Al_2O_3 (1.4 mg, 6.8×10^{-7} in Rh) in 2.5 mL of acetone and 5.0 mL of cyclohexene (4.94×10^{-2} mol, 73 000 maximum possible turnovers). At 1 h intervals, aliquots (≤0.05 mL) of the reaction solution were withdrawn from the ball valve of the Fischer−Porter bottle with a gastight syringe equipped with an 18 in. needle, all while under a continuous flow of H_2. Aliquots were removed only after the needle and syringe were thoroughly purged with H_2. Immediately after the aliquot was removed, 0.20 mL of a 2.5×10^{-5} M CS_2/acetone solution (0.007 equiv of CS_2/mol of *total* Rh) was injected into the reaction solution. The Fischer−Porter bottle was then purged an additional five times (15 s/purge) with hydrogen gas and repressurized to 40 ± 1 psig of H_2. The reaction solution

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(53) Jackson, S. D.; Munro, S.; Colman, P.; Lennon, D. *Langmuir* **2000**, *16*, 6519−6526.

(54) A control experiment, to ensure that the precatalyst, [(1,5-COD)Rh·$P_2W_{15}Nb_3O_{62}$]$^{8-}$, was completely converted into Rh(0) nanoclusters, was carried out, as detailed elsewhere[5,6] monitoring the reduction of Rh(I) to Rh(0) nanoclusters by GLC for the stoichiometric evolution of cyclooctane vs time (Figure L in the Supporting Information); the results indicate that the formation Rh(0) nanoclusters is complete after ∼15 h; hence, the use herein of >15 h in all experiments preforming the Rh(0) nanoclusters.

aliquot was then dissolved in 1 g (0.75 mL) of CD_2Cl_2 and examined by ^{1}H NMR. Plots of total turnovers vs both time (bottom axis) and the total equivalents of CS_2 added (top axis) are shown in Figure E of the Supporting Information. In addition, this experiment allows for the construction of a poison plot based on the "average rate" as calculated from the total number of turnovers that occurred over 1 h. A plot of poisoned average rate/initial average rate vs moles of CS_2/moles of *total* Rh in the hydrogenation of cyclohexene by 5% Rh/Al_2O_3 is shown in Figure F of the Supporting Information.

Two separate control experiments were also done to show that, as expected, single injections of 0.25 or 0.50 equiv of CS_2 (per mol *total* Rh) completely shut down the catalytic activity of the 5% Rh/Al_2O_3 catalyst for the hydrogenation of cyclohexene.

6. Additional Control Experiments. A. Test for Mass-Transfer Limitations (MTL). A control experiment was carried out with the catalyst that showed the fastest H_2 uptake in this study, 5% Rh/Al_2O_3, to ensure that the measured initial rates were not limited by the mass transfer of H_2 from the gas to the solution phase. Doubling the catalyst concentration resulted in doubling the initial rate ($\{-dH_2/dt\}_i = 50.8$ psig/h for 1.3 mg of catalyst vs $\{-dH_2/dt\}_i = 101.4$ psig/h for 2.6 mg of catalyst). This linear rate dependence upon the catalyst concentration requires that the observed initial rate is not influenced by mass-transfer limitations.

B. Test for the Reversible Poisoning of 5% Rh/Al_2O_3 by CS_2 under Our Experimental Conditions. In a drybox 2.5 mL of acetone and 5.0 mL of cyclohexene were added with separate 5 mL gastight syringes to 5% Rh/Al_2O_3 (1.3−1.4 mg) in a 2 dram vial. The reaction mixture was then transferred into a new 22 × 175 mm culture tube containing a new $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was then placed inside a Fischer−Porter bottle, sealed, transferred out of the drybox, placed in a 22.0 ± 0.1 °C water bath, and attached to the hydrogenation apparatus via the Swagelock quick-connects. Stirring was started (at >600 rpm), the Fischer−Porter bottle was purged 15 times with 40 ± 1 psig of H_2 (15 s/purge), and H_2 pressure in the Fischer−Porter bottle was set to 40 ± 1 psig. The reaction solution was then stirred for an additional 2 min, and $t = 0$ was set. Data was collected for 1 h, and an initial rate was calculated as described above. At this time either 0.20 or 0.50 mL of a 3.32×10^{-5} M CS_2 solution in acetone was added with a 1 mL gastight syringe to the Fischer−Porter bottle through the ball valve under a constant flow of H_2. The bottle was repressurized to 40 ± 1 psig, $t = 0$ was set, and pressure vs time data was collected for 1 h. After 1.5 h the bottle was repressurized again to 40 ± 1 psig and an additional set of data was collected. The repressurization and data collection were repeated once more. A plot of the relative rate vs time is shown in Figure 4 for both concentrations of CS_2 used. In each case, the initial rate of the poisoned catalyst did not change over a period of 6 h; this indicates that the dissociation of CS_2 from the surface, or any irreversible chemical transformation of it on the surface of the heterogeneous catalyst or the Al_2O_3 support, is negligible over this time period and, therefore, should not affect the poisoning studies described herein.

C. Test for the Reversible Poisoning of 5% Rh/Al_2O_3 by CS_2 in an Open System. A reaction solution was prepared as described above with 1.4 mg of catalyst, 2.5 mL of acetone, and 5.0 mL of cyclohexene in a Fischer−Porter bottle. The initial rate of the unpoisoned catalyst was determined as previously mentioned, $\{-dH_2/dt\}_i = 56.7$ psig/h. After the first hour of data collection the bottle was opened under a flow of H_2 and 0.200 mL of a 3.32×10^{-5} M CS_2 solution was added using a 500 μL gastight syringe. The bottle was purged two times (15 s/purge) and repressurized to 40 ± 1 psig. Pressure vs time data was collected for 1 h, and the initial rate of the poisoned catalyst was determined, $\{-dH_2/dt\}_i = 12.2$ psig/h (22% of the unpoisoned rate).

In an attempt to probe the stability of the poison on the catalyst surface (i.e., to probe whether or not the poison can be removed from the catalyst surface by purging with H_2), the Fischer−Porter bottle was purged 15 times (15 s/purge) and repressurized to 40 psig, and data was again collected for 1 h. This procedure was repeated three times, and finally, the reaction solution was vented to the atmosphere under a positive flow of H_2 for 2 min before the Fischer−Porter bottle was resealed and data was collected for a final 1 h. The results of these experiments are summarized in Figure 5 and indicate no recovery in the catalytic activity. These results imply that CS_2 binds very strongly to the catalyst surface and that, despite the poison's volatility (bp = 46 °C), it is not removed under our (mild) reaction temperature and conditions. In fact, CS_2 desorption from a catalyst surface has only been reported to occur at elevated temperatures (>52 °C),[23] values at least 30 °C greater than the experimental conditions used here.

D. Test for Reversible Poisoning of (40 ± 6 Å) Polyoxoanion-Stabilized Rh(0) Nanoclusters. A reaction solution was prepared as described above with 0.860 mL of a freshly prepared soluble Rh(0) nanocluster solution (3.58×10^{-4} M in Rh), 2.5 mL of acetone, and 5.0 mL of cyclohexene which were mixed in the drybox, transferred to a new culture tube, and placed in a Fischer−Porter bottle. Following removal of the Fischer−Porter bottle from the drybox and its attachment to the hydrogenation line, the initial rate of the unpoisoned catalyst was determined as previously mentioned ($\{-dH_2/dt\}_i = 23.3$ psig/h). After the first hour of data collection the bottle was opened under a positive flow of H_2 and 0.500 mL (or 0.300 mL in a subsequent experiment) of a 2.77×10^{-6} M CS_2/acetone solution was added with a 1 mL gastight syringe. The bottle was purged two times (15 s/purge) and repressurized to 40 ± 1 psig. Pressure vs time data was collected for 1 h, and the initial rate of the poisoned catalyst was determined. At preselected times thereafter, the same reaction solution was repressurized to 40 ± 1 psig of H_2 in the Fischer−Porter bottle and pressure vs time data was collected for 1 h periods. Pressure vs time data was then used to calculate initial rates of the poisoned catalyst as described above at the different, 1 h intervals. These initial rates (expressed relative to the unpoisoned initial rate) are plotted vs time in Figure I of the Supporting Information. The results show that the activity of the poisoned nanoclusers is not restored, results which require an irreversible interaction of the CS_2 poison with the nanocluster surface under the specified reaction conditions.

Note that the relative rate of the partially poisoned nanoclusters in Figure I decreases slightly over time. A control experiment was carried out to check if this reproducible decrease was due to a nonzero-order dependence on the decreasing concentration of cyclohexene. A reversibility experiment was set up as described above, except that after 6 h an additional 4.0 mL of cyclohexene was added to the reaction mixture (see the three rightmost squares in Figure I of the Supporting Information). Since no increase in rate was observed, the reaction must not be limited by (i.e., is effectively zero-order in) the cyclohexene concentration; therefore, the observed decrease in the relative initial rate vs time plot is likely due to a slow reaction of surface Rh with CS_2 (or CS_2-induced nanocluster agglomeration).

E. A Control Experiment Testing for Activity by the Polyoxoanion Alone as a Source of the Nonzero Rates Past the Intercepts in Figures 2 and 3. In a drybox 2.5 mL of acetone and 2.5 mL of cyclohexene were added with separate 5 mL gastight syringes to 2.0 mg of $[(C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ (3.2×10^{-7} mol) in a 2 dram glass vial. The reaction mixture was then transferred with a plastic pipet into a new 22 × 175 mm culture tube containing a new $^5/_8$ in. × $^5/_{16}$ in. Teflon-coated magnetic stir bar. The culture tube was then placed inside a Fischer−Porter bottle, sealed, transferred out of the drybox, placed in a 22.0 ± 0.1 °C water bath, and attached to the hydrogenation apparatus via the Swagelock quick-connects. Stirring was started (at >600 rpm), the Fischer−Porter bottle was purged 15 times with 40 ± 1 psig of H_2 (15 s/purge), and H_2 pressure in the Fischer−Porter bottle was set to 40 ± 1 psig. The reaction solution was then stirred for an additional 2 min, $t = 0$ was set, and pressure vs time data was collected for 1 h. No significant change in the pressure due to H_2 uptake was observed. This result shows that the polyoxoanion, $[(C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$, is not responsible for the nonzero activity observed at high CS_2/Rh(0) ratios in Figures 2 and 3.

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Supporting Information Available: Figure A: TEM of commercially available 5% Rh/Al_2O_3 (Strem). Figure B: Corrected H_2 pressure vs time plots for cyclohexene hydrogenation with 5% Rh/Al_2O_3 and varying amounts of CS_2 (12 experiments). Figure C: Control experiment demonstrating the absence of mass-transfer limitations (MTL). Figure D: Poisoning plot for cyclohexene hydrogenation catalyzed by 5% Rh/Al_2O_3 and poisoned with various amounts of a 1 day old solution of 3.32×10^{-5} M CS_2. Text: CS_2 poisoning of 5%Rh/Al_2O_3 monitored by ^{1}H NMR. Figure E: Plots of total turnovers, determined by ^{1}H NMR, of cyclohexene hydrogenation by 5% Rh/Al_2O_3 vs both time and vs total equivalents of CS_2 added per mole of *total* Rh. Figure F: Plot of poisoned average rate/initial average rate vs moles of CS_2/moles of *total* Rh, in the hydrogenation of cyclohexene by 5% Rh/Al_2O_3 as monitored by ^{1}H NMR. Figure G: Corrected H_2 pressure vs time plots for cyclohexene hydrogenation with polyoxoanion stabilized, 40 ± 6 Å Rh nanoclusters and varying amounts of CS_2 (17 experiments). Figure H: Corrected H_2 pressure vs time plots for cyclohexene hydrogenation with 5% Rh/Al_2O_3 and varying amounts of CS_2 in the presence of 1 equiv of $[(n\text{-}C_4H_9)_4N]_9[P_2W_{15}Nb_3O_{62}]$ per *total* Rh (14 experiments). Figure I: Plot of the relative rate (poisoned initial rate/unpoisoned initial rate) vs time for the hydrogenation of cyclohexene catalyzed by partially poisoned 40 ± 6 Å Rh(0) nanoclusters. The catalytic activity is not restored over time and, therefore, suggests that the CS_2 poison is irreversibly bound to the surface of the Rh(0) nanocluster under these reaction conditions. Figure J: Pressure change vs time for three independent acetone vapor correction control experiments. Text: Alternate addition method for the 5% Rh/Al_2O_3 poisoning experiment in which the CS_2 poison was added before exposure to H_2. Figure K: Plot of relative rate vs moles of CS_2/moles of *total* Rh for the hydrogenation of cyclohexene by 5% Rh/Al_2O_3 as monitored by the initial-rate method. Figure L: Plot of evolved cyclooctane vs time that accompanies the conversion of the precatalyst, $[(1,5\text{-COD})Rh\cdot P_2W_{15}Nb_3O_{62}]^{8-}$, to near-monodisperse, 40 ± 6 Å Rh(0) nanoclusters. This material is available free of charge via the Internet at http://pubs.acs.org.

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