

Oxidative Alkenylation of Arenes Using Supported Rh Materials: Evidence that Active Catalysts are Formed by Rh Leaching

Zhongwen Luo,^[a] Colby A. Whitcomb,^[b] Nicholas Kaylor,^[b, c] Yulu Zhang,^[a] Sen Zhang,^[a] Robert J. Davis,^{*[b]} and T. Brent Gunnoe^{*[a]}

This work focuses on the synthesis of supported Rh materials and study of their efficacy as pre-catalysts for the oxidative alkenylation of arenes. Rhodium particles supported on silica (Rh/SiO₂; ~3.6 wt% Rh) and on nitrogen-doped carbon (Rh/NC; ~1.0 wt% Rh) are synthesized and tested. Heating mixtures of Rh/SiO₂ or Rh/NC with benzene and ethylene or α -olefins and CuX₂ {X = OPiv (trimethylacetate) or OHex (2-ethyl hexanoate)} to 150 °C results in the production of alkenyl arenes. When

Introduction

Alkyl and alkenyl arenes are used as precursors for a range of high-value chemicals, including detergent precursors, plastics, elastomers and pharmaceuticals.^[1-5] For example, linear alkylbenzenes, which are primarily 2-aryl alkanes, serve as precursors alkylbenzene sulfonates - active components in for detergents.^[6] Styrene, one of the most important commodity chemicals, is used for polystyrene plastics and synthetic rubber manufacturing.^[7] The current industrial production of alkylbenzenes uses Friedel-Crafts or zeolite acid-based technologies.^[8] Two general technologies for styrene production, the ethylbenzene/styrene monomer process (EB/SM) and the propylene oxide/styrene monomer process (PO/SM), have been commercialized (Scheme 1).^[3,9–11] Although EB/SM and PO/SM processes have been commercialized, existing industrial processes for styrene and alkyl arene syntheses have some disadvantages, including: 1) multi-step processes; for example, the EB/SM process includes benzene alkylation, transalkylation, and ethylbenzene dehydrogenation, while the PO/SM process involves benzene alkylation, ethylbenzene oxidation, oxygen transfer, and dehydration; 2) energy-intensive operations such as trans-

[a]	Z. Luo, Y. Zhang, Prof. S. Zhang, Prof. T. B. Gunnoe
	Department of Chemistry
	University of Virginia
	Charlottesville, VA 22904 (USA)
	E-mail: tbg7h@virginia.edu
[b]	C. A. Whitcomb, Dr. N. Kaylor, Prof. R. J. Davis
	Department of Chemical Engineering
	University of Virginia
	Charlottesville, VA 22904 (USA)
	E-mail: rjd4f@virginia.edu
[c]	Dr. N. Kaylor
	Southwest Research Institute
	San Antonio, TX 78238 (USA)
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using Rh/SiO₂ or Rh/NC as catalyst precursor, the conversion of benzene and propylene or toluene and 1-pentene yields a ratio of anti-Markovnikov to Markovnikov products that is nearly identical to the same ratios as the molecular catalyst precursor [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂. These results and other observations are consistent with the formation of active catalysts by leaching of soluble Rh from the supported Rh materials.



Scheme 1. Industrial processes for styrene monomer production: EB/SM process (top) and PO/SM process (bottom).

alkylation and distillation; and 3) the inability to produce anti-Markovnikov products (*i.e.*, 1-aryl alkenes or alkanes).^[12] Thus, there is increased interest in developing new catalytic processes for direct arene alkenylation at a low operating temperature that offer anti-Markovnikov selectivity.^[13-15]

Transition metal-catalyzed arene alkenylation (*i.e.*, oxidative olefin hydroarylation) that functions by a pathway involving arene C–H activation and olefin insertion offers possible advantages over traditional acid-catalyzed arene alkylation (Scheme 2).^[14,16–20] These potential advantages include: a) direct arene alkenylation (rather than alkylation) via β -hydride elimination after the olefin insertion step, b) selective production of 1-aryl alkane/alkene by circumventing carbocationic intermediates that lead to Markovnikov selectivity, c) conversion of electron-deficient arenes, d) new regioselectivity for alkenyla-

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Scheme 2. Generic catalytic cycles for transition metal-catalyzed arene alkylation and alkenylation. $^{\left[14\right] }$

tion or alkylation of substituted arenes, and e) inhibition of polyalkylation since alkylated or alkenylated products can be less reactive than starting arenes.^[14] Molecular catalysts involving Ni, Ir, Ru, Pt, Pd and Rh have been studied for catalytic C–H alkylation or alkenylation of arenes with α -olefins.^[15,16,21-35]

Recently, we reported Rh-catalyzed arene alkenylation to directly synthesize styrene and 1-aryl alkenes using molecular catalysts in homogeneous processes.^[13,14,36-41] Based on the mechanistic studies, our initial proposed catalytic cycle involves (Scheme 3): a) Rh-carboxylate assisted arene C–H activation, b) ethylene coordination and insertion into a Rh-aryl bond, c) β -hydride elimination, and d) alkenyl arene dissociation and oxidation of a Rh–H intermediate with CuX₂ (X = carboxylate) to regenerate the starting catalyst. Under some conditions, we observed an induction period,^[13,36,37] which was proposed to be due to the rapid decomposition of the soluble Rh catalyst precursor to form insoluble Rh(s) followed by formation of the active catalyst through dissolution of Rh from the inactive Rh(0) species (Scheme 4).

In various Pd-catalyzed C–C coupling reactions, dissolution and re-adsorption of supported Pd pre-catalysts have been



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Scheme 3. General proposed reaction mechanism for Rh mediated styrene monomer synthesis.



Scheme 4. The proposed induction period pathway for Rh(I) mediated styrene synthesis using Cu(OAc)₂ as the oxidant, (X = carboxylate groups).^[37]

reported.^[42–49] For example, the Davis, Kohler and Jones groups used Pd catalysts supported on silica (Pd/SiO₂), zeolite (Pd/NaY), titania (Pd/TiO₂), and aluminum oxide (Pd/Al₂O₃) for Heck coupling reactions and found that dissolution of palladium is correlated with reaction rate.[42,46,49] The solid Pd catalyst functions as a reservoir for soluble Pd species (Scheme 5A). The agglomeration and redeposition of dissolved Pd species can also occur in the presence of supports such as SiO₂, Al₂O₃, and TiO₂, which forms Pd(0)/MO_x catalyst precursors (Scheme 5B).^[46,48,49] In the presence of phosphine ligands, it was proposed that aryl halides likely oxidize Pd(0) to form a molecular $L_n Pd^{II}(Ar)(X)$, (X = Br or Cl, L = phosphine) complex, which is proposed to participate in a Pd(II)/Pd(0) catalytic cycle (Scheme 5C).^[48,49]

As part of our efforts to delineate the dynamic between heterogeneous Rh and soluble Rh species for the oxidative alkenylation of arenes, we have prepared supported Rh species on silica (SiO_2) and nitrogen-doped carbon (NC) and studied their reactivity as catalyst precursors. Herein, we report the use of these supported Rh materials as a catalyst precursors for the synthesis of styrene and other alkenyl arenes with evidence





Scheme 5. General leaching/dissolution process (oxidation of Pd) to liberate soluble, active molecular palladium species (A), agglomeration or redeposition of Pd(0) (B), and main catalytic cycle (C).

that catalytic activity is a result of leaching of soluble Rh from the supported materials.

Results and Discussion

Synthesis of supported Rh materials. We prepared Rh nanoparticles supported on silica (Rh/SiO₂) using a modified ionexchange method.^[50,51] The weight loading of Rh was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis and found to be 3.6 wt%. Further characterization of Rh/SiO₂ was performed using transmission electron microscopy (TEM), dihydrogen chemisorption, and X-ray photoelectron spectroscopy (XPS). Dihydrogen chemisorption of the Rh/SiO₂ material indicated a metal dispersion of ~0.7 (H/Rh ratio), and the average metal particle size measured by TEM was found to be 2.2(5) nm (Figure 1, Table S1). The presence of metallic Rh(0) was confirmed with XPS, which showed a binding energy at 307.3 eV (Figure S1).^[37,52,53]

Nitrogen-doped carbon (NC) has been used as a support for single-atom catalysts with transition metals such as Co,^[54-56] Mn,^[54] Ni,^[54] Fe,^[54] Rh,^[57] and Pd.^[58] Supported Rh on nitrogendoped carbon (Rh/NC-HCl and Rh/NC-IWI) were prepared using a modified high-temperature thermal treatment as discussed in



Figure 1. HAADF-STEM image of synthesized Rh/SiO₂.

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detail in the experimental section.[55] The catalyst labeled as Rh/ NC-HCl was treated with aqueous HCl (in an attempt to remove metal particles) followed by a thermal treatment with H₂. The Rh/NC-IWI material was prepared using an incipient wetness impregnation (IWI) method for deposition of the Rh precursor Rh(NO₃)₃. According to ICP-OES analysis, the Rh loading was approximately 1.0 wt% for Rh/NC-HCl material and 1.5 wt% for Rh/NC-IWI. The Rh detected by ICP-OES analysis is associated with only the fraction of metal that could be removed from the sample for analysis. TEM characterization of the Rh/NC-HCl material showed Rh nanoparticles (Figure 2) with size of ~15(5) nm. The recovered Rh/NC-HCl catalysts after microwave digestion showed that some Rh nanoparticles could not be removed from the NC support, which suggests that some of the Rh nanoparticles are likely embedded inside the NC matrix (Figure S2). For the Rh/NC-HCl sample, XPS analysis of the N1s core level shows a broad envelop associated with multiple N species in the carbon matrix. Assuming only two types of sites for simplicity, quantitative analysis reveals about a 2:1 ratio of pyridinic sites (binding energy of ~398.3 eV) and graphitic sites (binding energy of ~400.8 eV) (Figure 3).^[55] TEM analysis of Rh/ NC-IWI showed the size of the Rh nanoparticles was ~ 20(4) nm (Figure 4).

Catalytic Arene Alkenylation using Rh/SiO₂ as Catalyst Precursor. We began our studies of catalysis using supported Rh materials with the conversion of benzene and ethylene to styrene using conditions that are similar to our previously



Figure 2. HAADF-STEM images of the synthesized Rh/NC-HCl material.



Figure 3. XPS characterization of N1s from Rh/NC-HCl showing at least two types of sites: 1) pyridinic sites at binding energy ~ 398.3 eV and 2) graphitic sites with binding energy ~ 400.8 eV.



Figure 4. HAADF-STEM images of the synthesized Rh/NC-IWI catalyst.



Next, we performed experiments to probe Rh leaching using ICP-OES measurement and the Maitlis' filtration test.^[49,59,60] During the styrene synthesis mediated by Rh/SiO₂ (conditions listed above), a Maitlis filtration using a 200 μ m filter at room temperature was performed after 12 h of reaction, which corresponded to 50(3)% conversion (based on Cu(II) as limiting reagent) of the reaction (Figure 5). We then tested the filtrate for catalytic activity. Under the same conditions used to test Rh/



Figure 5. Catalytic performance using Rh/SiO₂ for styrene synthesis without filtration (green), with addition of 500 eq. of PVPy (relative to surface Rh atoms) at time of zero for catalysis using Rh/SiO₂ (blue), and using the filtrate (solution) collected from a Maitlis filtration test at 12 h (red). Catalytic conditions: 5.3 mg Rh/SiO₂ material (0.00112 mmol), 15.5 mg PVPy, 10 mL benzene, 72 mg Cu(OPiv)₂ (240 eq. relative to surface Rh atoms), 20 eq. hexamethylbenzene as the internal standard, 40 psig ethylene and 150 °C.

SiO₂, we observed only a small amount of styrene production (Figure 5, red plot). The minimal catalytic activity of the filtrate is consistent with ICP-OES measurement of the filtrate (after Maitlis filtration) indicating that only approximately 1 mol% of the original amount of Rh from Rh/SiO₂ leached into the filtrate. In other published work, insoluble poly(vinylpyridine) (PVPy) has been used as a Pd(II) trap to confirm the leaching of Pd(II) from Pd catalyst on silica support.^[42,61-63] We performed similar trapping experiment to probe the possible leaching from catalysis using Rh/SiO₂. The addition of 500 equivalents of PVPy to the catalytic reaction using Rh/SiO₂ prevented the formation of styrene (Figure 5, blue plot), which is consistent with the hypothesis that the observed reactivity of Rh/SiO₂ might be from the leached and soluble Rh species. If it is assumed that catalytic styrene production using fresh Rh/SiO₂ is due to leached Rh, using the calculated apparent TOFs (~ $1.8(3) \times$ 10^{-2} s^{-1} for $[\text{Rh}(\mu-\text{OAc})(\eta^2-\text{C}_2\text{H}_4)_2]_2$ versus 5.0(3)×10⁻⁴ s⁻¹ for Rh/ SiO₂), we can estimate that approximately 3 mol% of the Rh from Rh/SiO₂ is solubilized. Given that this is an approximation, complicated by the dynamic nature of leaching, potential readsorption/trapping by the filter and standard deviations for TOF determinations, this estimate fits well with the 1% leaching determined by ICP-OES.

Using an α -olefin such as propylene for the arene alkenylation can result in multiple products depending on the regioselectivity of olefin insertion and selectivity of β -hydride elimination (Scheme 6). Using propylene and benzene coupling as a probe reaction, three "linear" products (or anti-Markovnikov products) and one "branched product" (Markovnikov product) are observed (Scheme 6). For benzene and propylene, we compared the regioselectivity using Rh/SiO₂ as catalyst precursor with [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂. Using Cu(OPiv)₂ as an oxidant, the L/B ratio (*i.e.*, the ratio of anti-Markovnikov to Markovnikov products) for Rh/SiO₂ mediated benzene and propylene coupling reactions was 10(2):1, which is statistically similar to L/ B selectivity (14(2):1) using [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ as a catalyst precursor under the identical conditions (Table S2). When Cu (OHex)₂ was used as an oxidant, statistically identical L/B



Scheme 6. Linear/branched product selectivity is dictated by the olefin insertion step and, in some circumstances, the relative rates of subsequent reactions (*i. e.*, Curtin–Hammett conditions).^[14]

selectivity was observed with 8.0(2):1 for Rh/SiO₂ and 7.4(1):1 for [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ (Table S3). These results are consistent with heterogeneous materials leaching an active catalyst similar to the species produced by the catalyst precursors Rh(μ -OAc) (η^2 -C₂H₄)₂]₂ and Rh/SiO₂.

Since CuX and HX (X = carboxylate) can be air-recycled to CuX₂ and H₂O, the Rh-catalyzed arene alkenylation has the potential to use catalytic amounts of Cu(II).³⁹ We have examined the reactivity of the Rh/SiO₂ catalyst precursor for aerobic styrene synthesis (1 atm air) and compared its aerobic catalytic performance in the presence and absence of Cu(OPiv)₂ (Figure S5). Heating Rh/SiO₂ in a mixture of benzene, 40 psig ethylene, 1 atm air, 100 eq. Cu(OPiv)₂ and 1000 eq. HOPiv at 150 °C, the supported catalyst precursor Rh/SiO₂ exhibits catalytic activity for styrene production. Compared with catalysis using stoichiometric Cu(II) oxidant, a 185(10) TO of styrene production was achieved at 100 h when 1 atm air was added (Figure S5). In the absence of Cu(II) salt using air as the sole oxidant, only 35(5) TO of styrene could be achieved after 104 h (Figure S5).

Impact of Carboxylate. Using Rh/SiO₂ as a catalyst precursor, catalysis using Cu(OHex)₂ is approximately three times more rapid than using Cu(OPiv)₂. Using Cu(OHex)₂ as an oxidant, we found that Rh/SiO₂ mediated styrene synthesis gave an overall yield of about 70(4)% {based on stoichiometric and limiting Cu(II)} after 8 h (Figure 6). Under similar conditions using Cu(OPiv)₂, Rh/SiO₂ catalysts gave a 65(3)% yield after 26 h (Figure S3). For the molecular precursor [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂, the *apparent* TOFs using Cu(OHex)₂ and Cu(OPiv)₂ are 3.0(2) × 10⁻² s⁻¹ and 1.5(2)×10⁻² s⁻¹, respectively, which is one to two



Figure 6. Catalytic performance (turnovers versus time plots) of styrene synthesis using fresh Rh/SiO₂ without isolation (black) and using recovered Rh/SiO₂ solid (centrifuge/separation methods used; orange). Reaction conditions: 10 mL benzene, 40 psig ethylene, 3.6 wt% Rh/SiO₂ (5.3 mg, 0.00112 mmol surface Rh atoms), 400 eq. Cu(OHex)₂ (relative to surface Rh atoms) at 150 °C. Note, another 400 eq. Cu(OHex)₂ is added at 3 h. Catalyst isolation and separation were conducted at 3 h and fresh benzene, 400 eq. Cu(OHex)₂, and ethylene were recharged.

orders of magnitude faster than when using Rh/SiO₂. During the Rh/SiO₂ and Cu(OHex)₂ mediated styrene production, a filtration test was conducted after 3 h of reaction. ICP-OES analysis of the filtrate from the reaction mixture confirmed that approximately 34% of Rh (compared with overall Rh amount on the silica support) leached from the silica support into solution. Evidently, more Rh leaches from Rh/SiO₂ when Cu(OHex)₂ is used as the oxidant (34% leaching of Rh) compared to the use of Cu(OPiv)₂ (~1%). The enhanced leaching of Rh with Cu (OHex)₂ likely explains the increased rate of styrene production using $Cu(OHex)_2$ versus $Cu(OPiv)_2$ when using Rh/SiO₂ as the catalyst precursor. Thus, the extent of Rh leaching appears to be dependent on the identity of the carboxylate ligand, which could be due to the difference in basicity or a steric effect. These results demonstrate that the oxidant {i.e., Cu(II)} and proligand (carboxylate) are important for the Rh leaching process.

Recycling of Rh/SiO₂. We tested the catalytic activity of recycled Rh/SiO₂ that was recovered from a styrene synthesis reaction after 3 h of reaction (Figure 6). Using this isolated Rh/SiO₂ material, we probed the conversion of benzene, ethylene and Cu(OHex)₂ to styrene at 150 °C. Figure 6 shows comparative reaction profiles using freshly made Rh/SiO₂ and the recovered Rh/SiO₂ material. A reaction using the recovered Rh/SiO₂ shows a longer induction period and slower rate of styrene production (Figure 6). In contrast, using the filtrate after 3 h of reaction using fresh Rh/SiO₂. Again, these results are consistent with the active catalyst being formed by leaching of Rh into solution.

Compared with an induction period of ~1 h when new Rh/SiO₂ is used for the styrene synthesis, the recovered Rh/SiO₂ material showed a longer induction period of ~12 h (Figure 6, note: the start time point for the recycled catalytic reaction is at 3 h in Figure 6). Although approximately 66% of the overall Rh species in the Rh/SiO₂ catalyst did not leach into the solution during the catalysis at 3 h (based on ICP-OES analysis, see above), the reactivity of recovered Rh/SiO₂ catalysts is substan-





Figure 7. Catalytic performance (turnovers versus time plots) for styrene synthesis using fresh Rh/SiO₂ without isolation (black) and using the recovered filtrate after centrifuge/separation test (red). Reaction conditions: 10 mL benzene, 40 psig ethylene, 3.6 wt% Rh/SiO₂ (5.3 mg, 0.00112 mmol surface Rh atoms), 400 eq. Cu(OHex)₂ (relative to surface Rh atoms), 20 eq. hexamethylbenzene as the internal standard and 150 °C. Note, another 400 eq. Cu(OHex)₂ is added at 3 h. Catalyst separation and isolation were conducted at 3 h. Then, the filtrate was recharged with 400 eq. of Cu(II) oxidant, and ethylene. The catalysis using the filtrate solution is shown in red with the starting time at 3 h.

tially reduced. One explanation for the long induction period observed with the recovered Rh/SiO₂ material is oxidation of Rh during the isolation of Rh/SiO₂ (which requires transferring out of and back into the glove box) following the initial catalytic reaction, which could inhibit leaching and/or catalysis. Thus, we probed dihydrogen reduction of the recovered Rh/SiO₂ material at 150 °C.^[64,65] The dihydrogen-treated, recovered Rh/SiO₂ exhibited similar reactivity compared with the recovered and untreated Rh/SiO₂ (Figure S6), which suggests that dioxygen does not deactivate the recovered Rh/SiO₂ catalysts.

We hypothesized that the Cu(II) salts might influence the catalysis in two roles (beyond serving as the oxidant): 1) Cu(II) likely oxidizes Rh(0) to form soluble catalyst, and 2) reduced Cu might be deposited on the Rh/SiO₂ material as the reaction proceeds, which could inhibit continued leaching of Rh into solution. TEM and XPS characterization of recovered Rh/SiO₂ material after 3 h of reaction were used to analyze possible copper deposition. Indeed, energy-filtered TEM mapping of copper on recovered Rh/SiO₂ (red and blue box regions in Figure 8) showed Cu deposition (bright spots within the blue box, Figure 8b) on the recovered solid (Figure 8). Moreover, XPS analysis of recovered Rh/SiO₂ confirmed Cu deposition with a binding energy of approximately 933 eV, which was attributed to Cu(I)/Cu(0) species (Figure S7).^[66-68]

When Rh/SiO₂ is pretreated in a benzene solution with 400 eq. Cu(OHex)₂ at 150 °C for 3 h, followed by charging with 40 psig ethylene, the catalytic performance of the Cu(II) pretreated Rh/SiO₂ (Cu(II)-pretreated Rh/SiO₂) showed about onethird of the activity compared to catalysis using fresh Rh/SiO₂ (Figure 9, blue). Separately, we treated Rh/SiO₂ with 2 bar dihydrogen and 200 eq. of Cu(OHex)₂ (relative to the amount of surface Rh) at 150 °C for 3 h assuming that reduced Cu(s) would be formed. Using this H₂/Cu-Rh/SiO₂ material for styrene synthesis, the rate of styrene formation is dramatically reduced compared with using fresh Rh/SiO₂ (Figure 9, yellow). These



Figure 8. TEM images of Rh/SiO₂ (a) recovered after 3 h of catalysis (Rh/SiO₂, Cu(OHex)₂, ethylene, benzene, 150 °C) and energy-filtered TEM map of copper at the recovered Rh/SiO₂ (b). Red box and blue box are the regions that energy-filtered TEM map of copper was examined with the bright spots on the right indicating copper.



Figure 9. Catalytic performance (turnovers versus time plot) of styrene synthesis using fresh Rh/SiO₂ (black), and Cu(II)-pretreated Rh/SiO₂ (blue), H₂/Cu-Rh/SiO₂ (yellow) and ethylene-benzene treated Rh/SiO₂ (orange). Reaction conditions: 10 mL benzene, 40 psig ethylene, 3.6 wt% Rh/SiO₂ (5.3 mg, 0.00112 mmol surface Rh atoms), 400 eq. Cu(OHex)₂ (relative to surface Rh atoms), 20 eq. hexamethylbenzene as the internal standard (relative to surface Rh atoms) and 150 °C. Note: another 400 eq. Cu(OHex)₂ is added at 3 h for the black plot.

results are consistent with the hypothesis that Cu deposition might inhibit Rh leaching from the Rh/SiO₂ material. Moreover, when a pretreatment of Rh/SiO₂ with 40 psig ethylene and benzene was carried out at 150 °C for 3 h before the addition of 400 eq. Cu(OHex)₂ salts (relative to the number of surface Rh atoms), catalytic reactivity was reduced substantially (Figure 9, orange). This result indicated that ethylene and/or benzene might also deactivate the Rh/SiO₂ catalyst.

Catalytic Arene Alkenylation using Rh/NC catalysts. In our effort to compare the impact of support on arene alkenylation using Rh nanomaterials as catalyst precursors, we prepared Rh materials supported by NC. The NC support has been demonstrated to stabilize supported transition metal catalysts.^[55,58,69-71] The synthesis and characterization of Rh-NC materials have been discussed above.

Using 1 wt% Rh/NC-HCl as the catalyst precursor with Cu $(OHex)_2$ as the oxidant for the conversion of benzene and ethylene (40 psig) to styrene at 150 °C, a short induction period of ~4 h was observed (Figure 10). After 28 h, a 35(3)% yield (relative to Cu(II) oxidant) was achieved. In the absence of the





Figure 10. Turnovers versus time plot using 1 wt% Rh/NC-HCl mediated styrene synthesis. Conditions: 10 mL benzene, 40 psig ethylene, 1 wt% Rh/ NC-HCl (13 mg, 0.00112 mmol Rh), 400 eq. Cu(OHex)₂ (relative to Rh measured through ICP-OES), and 20 eq. hexamethylbenzene (0.0224 mmol) as the internal standard at 150 °C.

Rh, the NC support showed no catalytic reactivity for styrene production through 38 h (Figure S8).

As described above for catalysis using Rh/SiO₂, we performed centrifuge and decanting experiments, which involved the isolation of solid Rh/NC-HCl material after 28 h and 72 h of reaction. We then probed catalysis with the recovered Rh/NC-HCl material for styrene production (Figure 11). After specific time points, these experiments involved centrifuging reaction solutions and decanting to separate insoluble materials from soluble filtrate species. Then, the recovered solid material was recharged with Cu(II), benzene and ethylene, heated to 150 °C and styrene production was quantified. In a representative experiment, we recovered and recycled insoluble Rh/NC-HCl twice (Figure 11). Catalytic cycles 2 and 3 show a slightly reduced styrene production rate (Figure 11). Compared with the ~4 h induction period when fresh Rh/NC-HCl is used, slightly longer induction periods (~8 h) were observed for both cycles 2 and 3 (Figure 11). In contrast to observations with Rh/



Figure 11. Catalytic turnovers versus time plots using Rh/NC-HCl as catalyst precursor for styrene synthesis: cycle 1 (0–28 h), cycle 2 (32 h–68 h), and cycle 3 (84 h–116 h). Reaction conditions: 10 mL benzene, 40 psig ethylene, 1 wt% Rh/NC-HCl (39 mg, 0.00336 mmol Rh), 400 eq. Cu(OHex)₂ (relative to Rh measured through ICP-OES), and 20 eq. hexamethylbenzene as an internal standard at 150 °C. Insoluble solid material was separated and recycled between each cycle with fresh benzene, Cu(II) oxidant, ethylene, and internal standard recharged.

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 SiO_2 (see above), the soluble materials in the filtrate from cycle 1 were not active for the styrene production (Figure S9).

Compared with overall Rh loading at the beginning of the catalysis, ICP-OES measurement of the recovered Rh/NC-HCl catalysts at 116 h (cycle 3) and the soluble filtrate Rh species/ solution (116 h) showed approximately 47% of the starting Rh loading and 0.4% of Rh in the solution (*i.e.*, the filtrate), respectively. The minimal leaching from the Rh/NC-HCl material is consistent with the result that the filtrate from Rh/NC-HCl is less active for styrene synthesis (Figure S9). In contrast, 34% Rh leaching was observed from Rh/SiO₂ mediated catalysis, which explains that the filtrate from Rh/SiO₂ catalyst is more active than the filtrate from Rh/NC-HCl.

The 1.5 wt% Rh/NC-IWI material was synthesized and characterized as described above. Large Rh nanoparticles (~ 20 nm) were observed in the Rh/NC-IWI material. We tested Rh/ NC-IWI as a catalyst precursor at conditions similar to those used to test Rh/NC-HCl (see above). The Rh/NC-IWI precursor showed no discernable induction period at the time scale studied (Figure 12). However, as shown in Figure 12, an isolation of solid Rh/NC-IWI catalysts were conducted in cycle 2 and 3, followed by recharging of fresh benzene, copper(II) and ethylene. The catalyst performance for styrene synthesis decreased in cycles 2 and 3 (Figure 12), which is gualitatively comparable with Rh-NC-HCl in Figure 11. An induction period of 2-4 h was also observed in these two cycles. This might indicate a possible continuous leaching from the solid Rh/NC-IWI. Compared with Rh/NC-HCl, catalysis normalized by Rh atom (measured by ICP-OES) using Rh/NC-IWI was much faster producing an 87(3)% yield (relative to Cu(II) oxidant) of styrene at 2 h (Figure 12) versus a 53(7)% yield (relative to Cu(II) oxidant) of styrene at 40 h (Figure 10).

In contrast to Rh/SiO₂ material, the insoluble solid materials using Rh/NC precursors could be recycled without substantial loss in activity or increased induction periods. The differences between Rh/SiO₂ and Rh/NC materials could possibly be explained by 1) the Rh/NC materials are active heterogeneous



Figure 12. Catalytic turnovers versus time plots using Rh/NC-IWI precursor mediated styrene synthesis: cycle 1 (0–2 h), cycle 2 (2 h–6 h), and cycle 3 (6 h–14 h). Reaction conditions: 10 mL benzene, 40 psig ethylene, 1 wt% Rh/NC-IWI (13 mg, 0.00112 mmol Rh), 400 eq. Cu(OHex)₂, (relative to Rh measured through ICP-OES), 20 eq. hexamethylbenzene as the internal standard (relative to Rh loading) at 150 °C. Insoluble solid material was separated and recycled between each cycle with fresh benzene, Cu(II) oxidant, ethylene, and internal standard recharged.



catalysts or 2) for Rh/NC materials the catalytic styrene production occurs by reversible leaching of soluble Rh into the solution under catalytic conditions. To further compare Rh/NC materials with soluble and molecular Rh catalysis, we compared regioselectivities for arene alkenylation using the α -olefins propylene and 1-pentene to quantify Markovnikov vs. anti-Markovnikov selectivity (Schemes 6 and 7). We assumed that if the Rh/NC material is a heterogeneous catalyst then different Markovnikov vs. anti-Markovnikov vs. anti-Markovnikov selectivity likely would be observed. Also, the use of toluene provides an opportunity to determine *ortho/meta/para* selectivity (Scheme 7).

Under identical catalytic conditions, the L/B selectivities induced from Rh/SiO₂, Rh/NC-HCl and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ for both benzene and propylene coupling and toluene and 1pentene coupling were examined. The L/B selectivities for benzene and propylene coupling are statistically identical for Rh/SiO₂, Rh/NC-HCl and the molecular Rh complex [Rh(µ-OAc) $(\eta^2 - C_2 H_4)_2]_2$ (Table 1). For coupling of benzene and propylene, the L/B selectivity observed with Rh/NC-HCl is 7.5(2), while Rh/ SiO₂ and molecular complex Rh(μ -OAc)(η^2 -C₂H₄)₂]₂ yield 8.0(2) and 7.4(1), respectively. Likewise, arene alkenylation using toluene and 1-pentene for Rh/NC-HCl, Rh/SiO₂ and $[Rh(\mu-OAc)$ $(\eta^2 - C_2 H_4)_2]_2$ catalysts gave statically identical L/B selectivities, 8.2(9):1, 10.4(2):1, and 9.9(6):1, respectively. Also, the meta/ para ratios for Rh/NC-HCl, Rh/SiO₂ and $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ catalysts are statistically identical at 1.7(1):1, 1.8(1):1, and 1.7(1):1, respectively (Table S5). Again, the statistically identical L/B selectivities observed from both supported Rh catalysts and molecular salt $[Rh(\mu-OAc)(\eta^2-C_2H_4)_2]_2$ likely indicates the same



Scheme 7. Rh/NC mediated linear/branched product selectivity for coupling reactions between toluene and 1-pentene with different *ortho*, *meta*, and *para* selectivity.

active Rh species, in which leaching and dissolution of supported Rh catalysts precursors forming soluble Rh catalysts possibly occur.

Conclusion

Supported Rh nanoparticles on silica $(3.6 \text{ wt% Rh/SiO}_2)$ and nitrogen-doped carbon (1 wt% Rh/NC-HCI and 1.5 wt% Rh/NC-IWI) were synthesized and characterized by TEM, XPS, and ICP-OES. The catalytic performances of supported Rh nanoparticles for styrene formation were tested and compared. In this work, we have demonstrated the leaching of 34% of the Rh/SiO₂ catalyst during styrene synthesis is likely due to the oxidation of reduced Rh upon reaction with Cu(II) salt. Further, the leached and soluble Rh is most likely the active catalyst for arene alkenylation. Although our studies indicate that the leaching of Rh forms the soluble and active catalyst, the nitrogen-doped carbon supports facilitate catalyst recycling. Compared with Rh/ SiO₂ catalyst, nitrogen-doped carbon supported Rh catalysts underwent a possible dissolution and re-adsorption process.

Experimental Section

General Methods. All reactions were performed under inert conditions employing standard Schlenk techniques or in a dinitrogen-filled glovebox unless specified otherwise. Glovebox purity was maintained by periodic dinitrogen purges and was monitored by a dioxygen analyzer (O_2 concentration was < 15 ppm for all reactions). Tetrahydrofuran (THF) was dried over potassium benzophenone ketyl under dinitrogen. Benzene was dried by passage through columns of activated alumina. Pentane was dried over sodium benzophenone ketyl. Benzene- d_6 was used as received and stored under a dinitrogen atmosphere over 4 Å molecular sieves. ¹H NMR spectra were acquired on a Varian Mercury 600 MHz spectrometer. All ¹H and ¹³C spectra are referenced against residual proton signals (¹H NMR) of deuterated solvents. GC/FID was performed using a Shimadzu GC-2014 system with a 30 mimes90.25 mm HP5 column with 0.25 µm film thickness. GC-MS was performed using a Shimadzu GCMS-QP2010 Plus instrument with a $30\ m\times 0.25\ mm$ SHRXI-5MS column with a $0.25\ \mu m$ thickness. Electron impact (El) ionization was used.

For sampling reaction mixtures in heated Fisher-Porter reactors, the reactors were allowed to cool to room temperature, sampled under dinitrogen, recharged with olefin, and reheated. Aliquots of the reaction mixture (<100 μ L) were analyzed by GC/FID using relative peak areas versus the internal standard (hexamethylbenzene). Styrene, allyl benzene, α -methyl styrene, trans- β -methyl styrene, and cis- β -methyl styrene production were quantified using linear

Table 1. L/B selectivity comparison of Rh/NC-HCl, Rh/SiO ₂ , and Rh(I) salt [Rh(µ-OAc)(η ² -C ₂ H ₄) ₂] ₂ mediated propylene and 1-pentene arene alkenylation.				
Catalysts ^[a] L	/B selectivity for benzene and propylene coupling	L/B selectivity for benzene and propylene coupling $^{\!$		
Rh/NC-HCI 7 Rh/SiO2 8 [Rh(μ -OAc)(η^2 -C2H4)2]2 7	7.5(2) 3.0(2) 7.4(1)	8.2(9) 10.2(2) 9.9(6)		

[a] Catalytic conditions: 10 mL benzene or toluene, 25 psig propylene, or 1000 eq. 1-pentene, 1 wt% Rh/NC-HCl (13 mg, 0.00112 mmol Rh), Rh/SiO₂ (5.3 mg, 0.00112 mmol Rh) or [Rh(μ -OAc)(η^2 -C₂H₄)₂]₂(0.00112 mmol Rh), 400 eq. Cu(OHex)₂ (relative to Rh), 20 eq. hexamethylbenzene as the internal standard (relative to Rh) and 150 °C. For the pentyl-products quantification, synthesized products are hydrogenated with 10 wt% Pd/C (10 mg) catalyst at 100 psig H₂ at room temperature overnight.

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regression analysis of gas chromatograms of standard samples of the authentic product. A plot of peak area ratios versus molar ratios gave a regression line using hexamethylbenzene (HMB) as the internal standard. For the GC/FID instrument, the slope and correlation coefficient of the regression lines were 1.67 and 0.99 (styrene), 0.87 and 0.99 (trans-stilbene), 1.40 and 0.99 (allylbenzene), 1.23 and 0.99 (α -methyl styrene), 1.47 and 0.99 (cis- β -methyl styrene), 1.38 and 0.99 (trans- β -methyl styrene), respectively.^[37] The turnover (TO) is defined as the product (i.e. styrene or linear alkenyl arenes) per catalyst site at any given time. The quantification of various tolyl-pentane products is performed by a reported GC-MS method.^[40] Briefly, for the 1-tolyl-1-pentane products, the slope and correlation coefficient of the regression lines were 1.34 and 0.998 (1-m-tolyl-1-pentane), 1.85 and 0.997 (1-p-tolyl-1-pentane) and 1.84 and 0.998 (1-o-tolyl-1-pentane), respectively. For decane, the slope and correlation coefficient were 2.08 and 0.998, respectively. The production of 2-tolyl-2-pentenes was quantified using the slope and correlation coefficient for a fit of cumene:n-propylbenzene, which enabled an approximation of the ratio of 1-tolyl-1-pentenes to 2-tolyl-2-pentenes. The slope and correlation coefficient of the regression line were 1.24 and 0.98 for cumene:n-propylbenzene, respectively. Ethylene and propylene were purchased in gas cylinders from GTS-Welco and used as received. Copper(II) 2ethylhexanoate was purchased from Sigma-Aldrich and used as received. Copper (II) pivalate and $Rh(\mu-OAc)(\eta^2-C_2H_4)_2$ was prepared according to literature procedures.⁷² All other reagents were purchased from commercial sources and used as received. Before catalysis, the supported Rh catalysts were treated with 2 bar of dihydrogen at 150 °C for 1 h. Caution: Mixtures of hydrocarbons and oxidants are potentially explosive. In these experiments, we took precautions to ensure safe mixtures and used pressure relief valves.

Rh/SiO₂ synthesis. Silica-supported Rh nanoparticle catalysts (Rh/ SiO_{2}) were prepared via an ion exchange method^[50,51] of the Rh precursor using Davisil 636 silica (Sigma-Aldrich) as support. RhCl₃ 3 h₂O precursor (0.250 g, 99%, Sigma-Aldrich) was dissolved in a solution of aqueous ammonia (5.5 mL ammonium hydroxide (14.8 M, 28%-30% of NH₃ in water), ACS plus, Fisher Scientific, in 282 mL distilled deionized water). The RhCl₃ solution was added dropwise over 10 min to 4.75 g of acid-washed Davisil 636 silica in 114 mL of distilled deionized water at 70 °C. The mixture was stirred for 60 min at 70 °C, and then cooled to room temperature. The mixture was washed with water and vacuum dried overnight. After calcination in flowing air (medical grade, GTS-Welco) at 400 °C for 2 h, the sample was reduced in flowing dihydrogen (99.999%, GTS-Welco) at 250 °C for 2 h. After reduction, the system was evacuated and cooled to 30 $^\circ\text{C}$ for analysis. At 30 $^\circ\text{C},$ the stoichiometric ratio of H to surface Rh is assumed to be 1:1. Using dihydrogen chemisorption on a Micromeritics ASAP 2020 adsorption system,⁵¹ the number of available metal sites was determined by extrapolating the linear portion of the isotherm to zero pressure with the assumption of no dihydrogen uptake on the support.

Rh/NC synthesis. Rhodium supported on nitrogen-doped carbon (Rh/NC-HCl) was prepared similar to a method reported previously.^[55,57,73] Carbon Black Pearls 2000 from Cabot Corporation was used as the carbon support. All of the other chemicals were purchased from Sigma-Aldrich Corporation. An aqueous solution of Rh(NO₃)₂ $3H_2O$ was mixed with an ethanol solution of 1,10-phenanthroline (Rh:phenanthroline molar ratio = 1:2) for 20 min at 80 °C. The mixture was added dropwise to a vigorously stirred slurry of carbon black in a 0.1 M NaOH aqueous solution at 80 °C for two hours. The slurry was then cooled, filtered, and thoroughly washed with DI water. The complex was then impregnated with an acetone solution of 80 wt% dicyandiamide relative to the complex, with vigorous stirring followed by drying at 70 °C overnight. The solid was then thermally treated at 700 °C for two hours under ultrahigh-

purity N₂ flow (100 mLmin⁻¹) with a ramp rate of 10 °Cmin⁻¹. A vigorously stirred, room-temperature, 1 M HCl solution was then used to remove any formed Rh nanoparticles from the surface. After the acid treatment, the solid was thoroughly washed with Dl water and dried overnight at 120 °C. Before use, the sample was heated at 10 °Cmin⁻¹ to 450 °C in ultrahigh-purity H₂ (100 mLmin⁻¹) and held at that temperature for 2 h. This catalyst has been labeled as Rh/NC-HCl. A metal-free nitrogen carbon catalyst (NC) was synthesized using an acetone solution of 0.4 g dicyandiamide impregnated into 0.5 g of carbon black using the same initial thermal treatment as the metal catalyst.

Additionally, a 1.5 wt% Rh/NC-IWI catalyst was synthesized using the NC support. A solution of 5 wt% Rh metal from an aqueous Rh $(NO_3)_2$ 6H₂O solution was impregnated onto the NC and subsequentially dried overnight at 120 °C. The solid was then heated to 450 °C with a ramp rate of 10 °C min⁻¹ in ultrahigh-purity H₂ flow (100 mLmin⁻¹) and held at that temperature for 2 h.

Transmission electron microscopy (TEM). Samples analyzed by transmission electron microscopy (TEM) were prepared by dispersing the powders in cyclohexane or hexanes (99.5%, anhydrous, Sigma-Aldrich) and sonicating for 1 minute before mounting on Au-supported holey carbon grids. The catalyst samples were imaged using an FEI Titan 80–300 operating at 300 kV. The Rh/SiO₂ sample was also characterized by an EDAX energy dispersive spectrometer (EDS) system in the scanning mode of TEM for single-nanoparticle composition analyses and elemental mapping. Lattice spacings were determined from selected-area electron diffraction and Fourier transforms of high-resolution TEM images.

X-ray photoelectron spectroscopy (XPS). The XPS was performed using a Phi VersaProbe III with a monochromatic Al K α X-ray source (1486.7 eV) and a hemispherical analyzer; instrument base pressure was ~ 10^{-7} Pa. Due to the air-sensitivity of Rh catalysts, a PHI vacuum transfer vessel (Model 04-111) was used to protect the sample from exposure to the ambient atmosphere during the transfer from the glovebox to the XPS analysis chamber. Thus, the entire procedure was performed without exposing the catalyst to air or moisture. An X-ray beam of 100 μm was utilized and was rastered over 1.4 mm to reduce the X-ray flux on the target. The electron-energy analyzer was operated with a pass energy of 55 eV for high-resolution scans with a 50 ms per step dwell time. Dualcharge compensation, using a low-energy flood gun with a bias of 1 eV and a low-energy Ar⁺ beam, was utilized during data acquisition. The Si 2p_{3/2} peak for SiO₂ (103.5 eV) and C1s (284.6 eV) peak were used as a binding energy reference for the spectra.

ICP-OES measurement. Quantitative elemental analyses for the supported Rh catalysts are carried out with inductively coupled plasma optical emission spectrometry (ICP-OES) on a PerkinElmer Avio-200 ICP spectrometer, and a microwave digestion method was developed based on a modified literature method.^[57] In a typical ICP sample preparation procedure, a certain amount of Rh sample (i.e. 10 mg Rh/SiO₂ or 13 mg of Rh/NC) and aqua regia (6 mL) are added in a quartz vessel. With the assistance of microwaves, the solution was heated at 180 °C for 7 min with a ramp rate of about 10°C/min. After cooling, the solution was transferred into a 10 mL tube. A fraction of the above solution (0.2 mL) was diluted in a 10 mL volumetric flask by the addition of 0.2 wt% HNO₂ solution. The concentration of Rh in the diluted solution was analyzed by ICP-OES. To certify the accuracy of this method, the digestion was compared to a reference sample analyzed by Galbraith Laboratories (2323 Sycamore Drive, Knoxville, TN 37921). The analytic results we measured are consistent with the results reported from Galbraith Laboratories.



Catalytic alkenylation of benzene with ethylene and propylene using Cu(X)₂ {(X = OPiv (trimethylacetate) or OHex (2-ethyl hexanoate)}. Representative catalytic reactions are described here. A stock solution containing $[Rh(\eta^2-C_2H_4)_2(\mu-OAc)]_2$ (0.011 mmol, 0.001 mol% of Rh relative to benzene) or equivalent amount solid Rh catalysts:Rh/SiO₂, Rh/NC-HCl or Rh/NC-IWI, hexamethylbenzene (0.046 g, 0.23 mmol), and benzene (10 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with 10 mL solution of benzene and copper salt (400 eq. per Rh, 4.4 mmol). The vessels were sealed, pressurized with ethylene (40 psig) or propylene (25 psig), and subsequently stirred and heated to 150 °C. For the catalysis with ethylene, the reactions were sampled every 2 or 4 h. With propylene, the reactions were sampled when the solution turned yellowish brown and Cu oxidant was consumed.

Catalytic alkenylation of toluene with 1-pentene using Cu(OHex)₂ (OHex (2-ethyl hexanoate)). A stock solution containing [Rh(η^2 - $(C_2H_4)_2(\mu$ -OAc)]₂ (0.011 mmol, 0.001 mol% of Rh relative to benzene) or equivalent amount solid Rh catalysts: Rh/SiO₂, Rh/NC-HCl or Rh/ NC-IWI, hexamethylbenzene (0.046 g, 0.23 mmol), and toluene (10 mL) was prepared in a volumetric flask. Fisher-Porter reactors were charged with 10 mL solution of toluene, 1000 eq. 1-pentene (relative to Rh), copper salt (400 equiv. relative to per Rh, 4.4 mmol). The vessels were sealed and pressurized with nitrogen (50 psig), and subsequently stirred and heated to 150 °C. For the catalysis evaluation of supported Rh catalysts, the reactions were sampled every 4 h. The products quantification is determined after hydrogenation of the unsaturated products. The hydrogenation procedure was adopted from the literature⁴⁰ and it was performed at room temperature using 10% Pd/C catalyst under 100 psig hydroaen pressure.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Rhodium \cdot Styrene \cdot Alkenyl Arenes \cdot Leaching \cdot Readsorption

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Alkenylation of arenes: For the oxidative arene alkenylation reactions, our study using various supported Rh catalysts indicates possible leaching of oxidized Rh into solution to form the soluble and active catalyst. The leaching of Rh is likely due to the oxidation of reduced Rh upon reaction with Cu(II) carboxylate. Compared with Rh/SiO₂ catalyst, nitrogen-doped carbon (NC) supported Rh catalysts (Rh/NC) underwent a possible dissolution and reabsorption process. Z. Luo, C. A. Whitcomb, Dr. N. Kaylor, Y. Zhang, Prof. S. Zhang, Prof. R. J. Davis*, Prof. T. B. Gunnoe*

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Oxidative Alkenylation of Arenes Using Supported Rh Materials: Evidence that Active Catalysts are Formed by Rh Leaching