



Arene hydrogenation using supported rhodium metal catalysts prepared from $[\text{Rh}(\text{COD})\text{H}]_4$, $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$, and $[\text{Rh}(\text{COD})\text{Cl}]_2$ adsorbed on SiO_2 and Pd-SiO_2

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Abstract

Four different rhodium precursors, $[\text{Rh}(\text{COD})\text{H}]_4$, $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$, $[\text{Rh}(\text{COD})\text{Cl}]_2$, and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, adsorbed onto silica (SiO_2) or onto palladium supported on silica (Pd-SiO_2), were examined for their catalytic arene hydrogenation activities. Rates of toluene hydrogenation were compared when the catalysts were pretreated with hydrogen as follows: none, 40°C for 24 h, and 200°C for 4 h. With no hydrogen pretreatment, the rhodium precursors adsorbed on Pd-SiO_2 showed higher activities than the corresponding precursors on only SiO_2 . As the hydrogen pretreatment temperature was increased, the activities of the catalysts on SiO_2 increased; the highest activity occurred with catalysts pretreated at 200°C . Conversely, milder pretreatments were more effective for the catalysts on Pd-SiO_2 ; higher temperature pretreatments reduced activities. The catalysts were characterized by their activities, diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). All of the studies indicate that the active catalytic species is rhodium metal. On silica, H_2 reduction of the rhodium complex to Rh metal under arene hydrogenation conditions was slow in all cases except $[\text{Rh}(\text{COD})\text{H}]_4$. However, on Pd-SiO_2 , the palladium accelerated the reduction of all of the Rh complex precursors to rhodium metal under the same conditions. The resulting Rh-Pd-SiO_2 bimetallic catalysts exhibited higher activities than catalysts of the same composition prepared by classical methods.

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1. Introduction

Our group has shown that catalysts consisting of tethered complexes on supported metals (TCSM) are effective catalysts for various hydrogenation reactions [1–5]. In particular, TCSM catalysts (Fig. 1) that contain a rhodium complex tethered to silica that also has supported palladium metal are highly active for the

hydrogenation of arenes under mild conditions (1 atm, 40°C) [1–5]. Both the tethered rhodium complex and supported palladium contribute to the high activities of the catalysts. Their activities are much greater than either the complex tethered to silica or palladium on silica separately. The specific roles of the tethered complex and supported palladium are not known, but it was suggested, by our group [1–5], that the increased activity is due to hydrogen activation by the palladium, hydrogen spillover [6] to the silica surface, and utilization of the activated hydrogen by the tethered rhodium catalyst. Another possibility is that the activity of the

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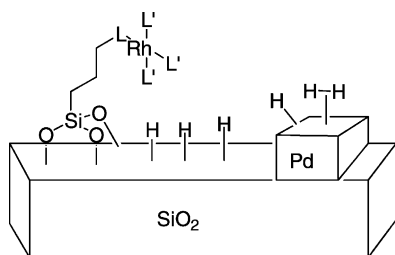


Fig. 1. Conceptual illustration of a TCSM catalyst consisting of a tethered homogeneous complex on a supported metal heterogeneous catalyst.

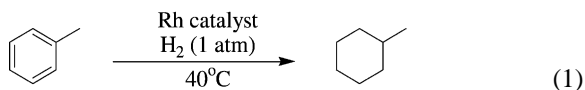
TCSM catalyst is due to rhodium metal on the silica which is formed by palladium-promoted reduction of rhodium that dissociates from the tethered complex. One goal of the work described in the present paper was to determine whether palladium promotes the formation of rhodium metal in catalysts that are prepared by adsorbing Rh complexes on Pd-SiO₂.

In the literature, there are reports of rhodium-palladium bimetallic catalysts on silica or alumina supports that exhibit behavior opposite to that of the TCSM systems. Papers by del Angel et al. [7] and Araya et al. [8] show that supported bimetallic rhodium-palladium catalysts prepared by impregnation of RhCl₃ and PdCl₂ in aqueous solutions or bis(acetylacetonato)palladium in dichloromethane onto silica or alumina are less active for benzene hydrogenation than rhodium-only supported catalysts [7,8]. In contrast, TCSM catalysts with tethered rhodium complexes and supported palladium metal are more active for arene hydrogenation than catalysts consisting of the tethered rhodium complexes only [1–5]. Therefore, we have investigated conditions under which palladium increases or decreases the arene hydrogenation activity of rhodium catalysts.

Silica- and alumina-supported rhodium is known to be much more active than supported palladium as an arene hydrogenation catalyst [7–9]. The activity of the palladium-supported catalyst is known to be structure insensitive and does not depend on the size of the palladium particles [9]. On the other hand, the activity of supported rhodium catalysts is structure sensitive and depends on particle size. Rhodium metal clusters of 10 Å or larger are needed for arene hydrogenation; smaller particles show no arene hydrogenation activity [9–12].

Considering the structure sensitive nature of supported rhodium catalysts, we also describe in this report variations in activities of catalysts prepared from different types of rhodium complexes. Thus, the following four rhodium complexes were examined: RhCl₃·3H₂O, [Rh(COD)Cl]₂ [13], [Rh(COD)₂]⁺BF₄[−] [14], and [Rh(COD)H]₄ [15,16]. RhCl₃·3H₂O was chosen as a Rh catalyst precursor because it is commonly used for the preparation of supported rhodium metal catalysts by the incipient wetness impregnation method. It is reduced to metallic rhodium on silica surfaces by exposure to hydrogen gas above 200 °C [17]. [Rh(COD)Cl]₂ is frequently used as a starting material for the synthesis of homogeneous rhodium hydrogenation catalysts [13], and was chosen for these studies as a model of surface species that may result from decomposition of rhodium halide catalysts. Also, Blum and coworkers [18] showed that a sol-gel-entrapped [Rh(COD)Cl]₂ becomes an active arene hydrogenation catalyst if metallic palladium is present in the sol-gel matrix. The authors suggested the activity of these catalysts arose from a synergy facilitated by the close proximity of the rhodium and palladium in the matrix. The cationic [Rh(COD)₂]⁺BF₄[−] is frequently used to prepare homogeneous rhodium hydrogenation catalysts [14] and is a precursor for a number of tethered catalysts on silica [1–5,19,20]. In addition, the very similar [Rh(COD)(PhCN)₂]⁺ClO₄[−] is reduced to metallic rhodium under hydrogenation conditions of 25–100 °C in methanol, methylene chloride, or in the solid state [21]. Finally, [Rh(COD)H]₄, which catalyzes the hydrogenation of toluene at room temperature (AR = 0.11 mol MeCy/(mol Rh min)), is reduced to rhodium nanoclusters, with an average size of 2 nm, under the reaction conditions [16].

For the studies reported here, the RhCl₃·3H₂O catalysts were prepared by the standard impregnation method, while the other catalysts were synthesized by adsorbing the rhodium complexes onto silica (SiO₂) or palladium supported on silica (Pd-SiO₂) under conditions (refluxing toluene for 4 h) similar to those used in the synthesis of TCSM catalysts [1–5,20]. These catalysts were examined for their activities in toluene hydrogenation, under mild conditions of 1 atm H₂ and 40 °C (Eq. (1)).



(1)

Sometimes the catalysts were studied without pretreatment; at other times, they were pretreated with hydrogen at 40 °C for 24 h or 200 °C for 4 h. The 40 °C hydrogen pretreatment was chosen to reflect conditions that would be present under prolonged hydrogenation reaction times (Eq. (1)). The 200 °C hydrogen pretreatment was chosen to simulate conditions used in the production of Rh-SiO₂ from RhCl₃·3H₂O. The catalysts were also characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. General considerations

The following chemicals were purchased: RhCl₃·3H₂O from Pressure Chemicals, PdCl₂ from DFG, silica (SiO₂) Merck grade 10184 (BET surface area, 300 m² g⁻¹; pore size 100 Å) and 1,5-cyclooctadiene (COD) from Aldrich. Toluene and methylene chloride were dried prior to use by passage through an alumina column under argon [22]. The following compounds were prepared by literature methods: [Rh(COD)Cl]₂ [13], [Rh(COD)₂]⁺BF₄⁻ [14], and [Rh(COD)H]₄ [16]. The preparation of Pd-SiO₂ (Pd, 10 wt.%) was described previously [1].

FTIR and diffuse reflectance infrared Fourier transform spectroscopy spectra were obtained on a Nicolet 560 spectrophotometer. The main compartment, equipped with a TGS detector, was used to take solution IR spectra using a NaCl solution cell. An auxiliary experiment module (AEM) containing a Harrick diffuse reflectance accessory with a MCT detector was used to obtain the DRIFT spectra of solid samples. Gas chromatographic analyses were performed on a Hewlett-Packard HP 6890 GC using a 25 m HP-5 capillary column attached to a FID detector. Rhodium content of the supported catalysts was determined by ICP-AES conducted by MPC Analytical Services of the Ames Laboratory. Samples for analysis were prepared by dissolving a 50 mg sample in 5.0 ml of aqua regia at 90 °C, then 5.0 ml of 5% aqueous HF was added and the mixture was heated to the same temperature. The resulting solution was diluted to 25 ml in a volumetric flask. Experimentally determined rhodium

compositions (w/w) are listed for representative catalysts in the following sections.

2.2. Preparation of arene hydrogenation catalysts

2.2.1. Preparation of silica-supported metal catalysts (M-SiO₂; M = Rh)

Rh-SiO₂: The preparation of Rh-SiO₂ was similar to that reported in the literature [17]. To 0.234 g of RhCl₃·3H₂O dissolved in 20 ml of water, was added 5.0 g of SiO₂ with stirring. After stirring overnight at room temperature, water was removed with a rotary evaporator at 80 °C. The solid was then dried further in an oven at 110 °C overnight. The sample was then placed in a tube furnace, treated with a N₂ flow, and heated to 200 °C for 2 h under the N₂ flow. The sample was cooled to room temperature under N₂, and the gas flow was switched to H₂. Then the sample was reduced for 3 h in a H₂ flow at 200 °C before the temperature was ramped to 250 °C for an additional 5 h. The resulting black solid, Rh-SiO₂, was collected after it had been allowed to cool under H₂ to room temperature (Rh, 1.17 wt.%).

2.2.2. Preparation of silica-supported bimetallic catalysts (M-M'-SiO₂; M, M' = Pd or Rh)

Rh-(Pd-SiO₂): These catalysts were produced following the procedure for the preparation of Rh-SiO₂ (given above) using Pd-SiO₂ instead of SiO₂ (Rh, 1.65 wt.%; Pd, 10 wt.%).

Rh/Pd-SiO₂: This catalyst was prepared by the coimpregnation of Rh and Pd. First, 4.6 g of SiO₂ was allowed to stir overnight in an aqueous solution of PdCl₂ (1.0 g, 5.4 mmol) and RhCl₃·3H₂O (0.20 g, 0.90 mmol) in 30 ml of 0.2 M HCl. After rotary evaporation at 80 °C and oven drying at 110 °C overnight, the sample was placed in a tube furnace, where it was reduced in a H₂ flow at 450 °C for 5 h (Rh, 1.46 wt.%; Pd, 10 wt.%).

Rh/Pd(O₂)-SiO₂: This catalyst was prepared by the coimpregnation of Rh and Pd by stirring 4.6 g of SiO₂ overnight in an aqueous solution of 1.0 g (5.4 mmol) of PdCl₂ and 0.20 g (0.90 mmol) of RhCl₃·3H₂O in 30 ml of 0.2 M HCl. After rotary evaporation at 80 °C and oven drying at 110 °C overnight, the sample was placed in a tube furnace and calcined in an air flow at 500 °C for 6 h, before being reduced in an H₂ flow at 500 °C for 6 h (Rh, 1.56 wt.%; Pd, 10 wt.%).

Pd-(Rh-SiO₂): This catalyst was prepared by sequential addition of the metals following a literature preparation [8]. A solution of 23 mg (75 μmol) of bis(acetylacetonato)palladium in 5 ml of CH₂Cl₂ was stirred for 1 h with 1.0 g of 0.16% Rh-SiO₂. After vacuum drying, the sample was reduced at 450 °C in a flow of H₂ for 5 h (Rh, 0.16 wt.%; Pd, 0.80 wt.%).

2.2.3. Preparation of adsorbed rhodium complexes on SiO₂ and Pd-SiO₂

2.2.3.1. General procedure. Catalysts were prepared by placing 97 μmol of the rhodium complex and 0.50 g of SiO₂ in a round bottom flask that was attached to a reflux condenser further linked to a Schlenk line. The atmosphere in the apparatus was replaced with nitrogen; 20 ml of toluene and 5.0 ml of CH₂Cl₂, for solubility, were added; and the system was refluxed for 4 h. The mixture was cooled to room temperature and stirred further for 12 h at room temperature. Finally, the solvent and unadsorbed species were filtered off, and the remaining solid was washed at least three times with 20 ml of toluene or until the toluene washings were clear.

The resulting adsorbed catalysts and rhodium contents, determined by ICP-AES, are listed below:

Adsorbed catalysts	Rhodium contents (wt.%)
[Rh(COD)Cl] ₂ -SiO ₂	Rh, 0.093
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂	Rh, 1.68
[Rh(COD)H] ₄ -SiO ₂	Rh, 1.68
[Rh(COD)Cl] ₂ -Pd-SiO ₂	Rh, 0.44; Pd, 10
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂	Rh, 1.56; Pd, 10
[Rh(COD)H] ₄ -Pd-SiO ₂	Rh, 1.84; Pd, 10

2.2.4. Hydrogen pretreatment of adsorbed catalysts

Treatment at 40 °C: The catalyst (100 mg) was placed in a jacketed vessel, described in Section 2.3, with a stir bar. The atmosphere was replaced with hydrogen by performing a series of three vacuum/hydrogen flushes. Under a hydrogen atmosphere (1 atm) in the absence of solvent, the temperature was raised to 40 °C. The dry catalyst was allowed to stir for 24 h at 40 °C under hydrogen. Then, the temperature was lowered to room temperature; the hydrogen atmosphere was removed under vacuum and replaced with nitrogen; and the sample was collected

and stored under nitrogen. The resulting catalysts are:

- [Rh(COD)Cl]₂-SiO₂/40 °C;
- [Rh(COD)Cl]₂-Pd-SiO₂/40 °C;
- [Rh(COD)₂]⁺BF₄⁻-SiO₂/40 °C;
- [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C;
- [Rh(COD)H]₄-SiO₂/40 °C;
- [Rh(COD)H]₄-Pd-SiO₂/40 °C.

Treatment at 200 °C: The catalyst (100 mg) was placed in a tube furnace. The atmosphere was replaced with hydrogen using three vacuum/hydrogen flush cycles. Then, hydrogen was passed over the sample for 15 min at room temperature before the temperature was ramped to 200 °C. Hydrogen flow was continued at 200 °C for 4 h. Then, the sample was cooled to room temperature; the atmosphere was switched to nitrogen; and the sample was collected and stored under nitrogen. The resulting catalysts are:

- [Rh(COD)Cl]₂-SiO₂/200 °C
- [Rh(COD)Cl]₂-Pd-SiO₂/200 °C
- [Rh(COD)₂]⁺BF₄⁻-SiO₂/200 °C
- [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C
- [Rh(COD)H]₄-SiO₂/200 °C
- [Rh(COD)H]₄-Pd-SiO₂/200 °C

2.3. Hydrogenation reactions

2.3.1. Hydrogenation of toluene

A standard hydrogenation run consisted of placing 50 mg of catalyst (~10 μmol of Rh) into a three-neck jacketed vessel containing a Teflon-coated stir bar (Fig. 2). One neck of the reaction vessel was capped with a glass stopper. The center neck was fitted with a rubber and Teflon septum to allow for input of solvents and removal of GC samples via syringe. The third neck was fitted with a three-arm “Y” stopcock. This allowed the reaction vessel to be attached to a vacuum/argon Schlenk line and the burette to be filled with hydrogen.

After the catalyst was placed in the reaction vessel, the atmosphere in the reaction flask was replaced with Ar using three vacuum/flush cycles. Next, the jacket of the vessel was attached to a constant temperature bath and the temperature was raised to 40.0 °C (±0.2 °C). While the temperature was being achieved, the hydrogen gas reservoir was filled through a series

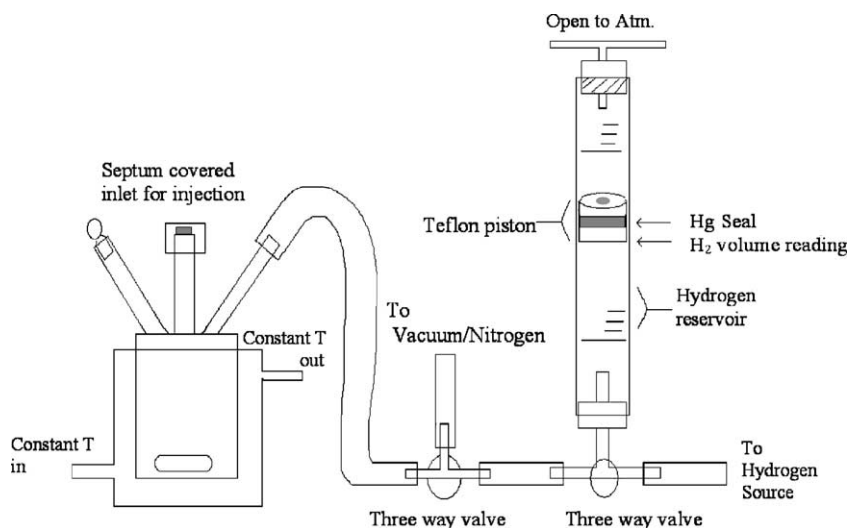


Fig. 2. Hydrogenation apparatus.

of three consecutive vacuum and hydrogen gas flush cycles. After the temperature had stabilized at 40 °C and the gas burette was full of hydrogen, the reaction vessel itself was evacuated and filled with hydrogen three times. Immediately after replacing the nitrogen atmosphere with hydrogen, 5.0 ml of toluene were added via syringe. The reaction was opened to the hydrogen gas reservoir and stirring was initiated. Generally, less than 5 min were required for the toluene to warm to 40 °C and for the burette to stabilize after addition of solvent to the reaction vessel; after this time, hydrogen uptake readings were made. The rate of reaction was monitored by the volume of hydrogen taken up with time. In all cases, methylcyclohexane (MeCy) was the only product observed, and hydrogen uptake readings from the burette matched the amount of MeCy product determined by GC analysis. Solvent and reaction vessel volumes were the same for all runs. The stirring speed (600 rpm) was held constant in the reported reactions, but changes in stirring speeds (300–1200 rpm) did not change the observed rates indicating that effects of hydrogen mass transfer were not significant and rates were not diffusion limited. Rates were calculated as atomic rates (AR) [23] based on the total moles of methylcyclohexane produced (1/3 of the moles of hydrogen gas consumed) divided by the moles of rhodium in

the catalyst and the time of the reaction in minutes, Eq. (2).

$$\text{AR} = \frac{\text{total moles of methylcyclohexane produced}}{\text{total moles of Rh in the catalyst (min)}} \quad (2)$$

2.3.2. Hydrogenation of 1-hexene

The same hydrogenation setup and procedure used for toluene hydrogenation were utilized with the following modifications. The amount of catalyst was reduced to 25 mg (~5 μmol of Rh); the temperature was held at 0.0 °C (±0.2 °C); and 1-hexene (5.0 ml) was used as both solvent and substrate. Rates, as atomic rates [23], were calculated as in Eq. (2), but based on the total moles of hexane produced (the same as the number of moles of hydrogen gas consumed).

2.3.3. Hydrogenation in the presence of mercury

After initial rates of hydrogenation of toluene or 1-hexene were determined, 0.2 ml (14 mmol) of Hg was added to the reaction via syringe. The rate of hydrogen uptake was continuously monitored. In cases where the effect of mercury on the rate was not complete in 1 h, the hydrogen atmosphere was replaced with argon and the mercury was stirred

with the catalyst under the inert atmosphere of argon for a period of time. After this time (2 or 17 h), the argon atmosphere was replaced with hydrogen via three quick vacuum/hydrogen flush cycles, and rates of the mercury-treated reactions were measured by following the hydrogen uptake with time.

2.4. IR studies of CO treated catalysts

The catalyst (50 mg) was placed in 1.0 ml of toluene and stirred under 1 atm of CO for 18 h. The samples were then filtered, washed three times with 1.0 ml of toluene, and vacuum dried before being analyzed by DRIFTS.

2.5. TEM analysis of catalysts

Samples were crushed using an agate mortar and pestle. The finely separated samples were then floated using methanol over a holey carbon grid supported on a copper grid. The samples were air dried and then analyzed with a Philips CM 30 transmission electron microscope equipped with a LINK energy dispersive spectrometer (EDS) system. Both selected-area electron diffraction (SAED) and micro-diffraction patterns were obtained from the samples for phase identification. Visual images were manipulated with Photoshop and distances measured with Image-Pro Plus[®]. In order to obtain accurate statistical results of size distribution of nano particles, more than 120 particles were measured for analysis. MS Excel was used to tabulate distances and produce distribution curves.

2.6. XPS analysis of catalysts

Samples were heated to 150 °C under vacuum for 12 h prior to analysis. The samples were then mounted on two-sided tape and analyzed with a Physical Electronics 5500 Multi-technique system using the standard Mg source. An initial survey was conducted from the range 0–1100 eV and then multiple elemental regions were examined including Rh, Pd, C, Si, and O regions. Physical Electronics' MultiPak[®] software was used to analyze the data. For all samples, peaks were referenced to C (1s, 284.5 eV) and/or Si (2p, 103.3 eV).

3. Results

3.1. Activities of [Rh(COD)H]₄-based catalysts

The rates of toluene hydrogenation to methylcyclohexane at 40 °C under 1 atm of H₂ in the presence of [Rh(COD)H]₄-based catalysts are summarized in Table 1. In solution, [Rh(COD)H]₄ is active from the outset (AR = 1.83 min⁻¹) (entry 1). When adsorbed onto silica, [Rh(COD)H]₄ activity (entry 2) appears to increase with time, as is evident in the higher rate at 6 h (AR = 2.26 min⁻¹) than at 1 h (AR = 1.59 min⁻¹); in contrast, the activity of [Rh(COD)H]₄ in solution decreases with time. Hydrogen pretreatments enhance the activity of the silica-supported catalyst. Pretreatment at 40 °C (entry 3) causes the initial activity to nearly double (AR = 3.33 min⁻¹) and to remain elevated even after 6 h (AR = 2.64 min⁻¹). A 200 °C pretreatment (entry 4) causes the initial rate to triple (AR = 5.13 min⁻¹) and remain high even after 6 h (AR = 4.17 min⁻¹).

The catalyst [Rh(COD)H]₄-Pd-SiO₂ consisting of [Rh(COD)H]₄ adsorbed onto Pd-SiO₂ shows high activity from the outset, AR = 4.80 min⁻¹ (entry 5). For this system, hydrogen pretreatments provide no benefit. A 40 °C pretreatment (entry 6) slightly decreases the activity (AR = 3.77 min⁻¹), and a 200 °C pretreatment reduces the activity by a factor of nearly five (AR = 1.07 min⁻¹) (entry 7).

3.2. Activities of [Rh(COD)₂]⁺BF₄⁻-based catalysts

Rates of toluene hydrogenation for [Rh(COD)₂]⁺BF₄⁻-based catalysts are summarized in Table 1. The cationic [Rh(COD)₂]⁺BF₄⁻ is insoluble in toluene; when it is dissolved in a 1:4 (v/v) mixture of CH₂Cl₂:toluene, the resulting solution is only weakly active (AR = 0.02 min⁻¹) (entry 8). The silica-supported catalyst [Rh(COD)₂]⁺BF₄⁻-SiO₂ (entry 9) requires a long induction period, ~1 day, before achieving a steady AR of 0.67 min⁻¹, which is maintained for over 3 days. If this catalyst is pretreated with H₂ at 40 °C, it shows an increased initial rate (AR = 1.58 min⁻¹) (entry 10) that decreases to a steady AR of 0.67 min⁻¹ after 10 h. In contrast, 200 °C pretreatment provides a highly active catalyst,

Table 1
Rates of toluene hydrogenation to methylcyclohexane^a

Entry	Catalyst	AR ^b (1 h)	AR ^b (6 h)	AR ^b (Xh)
1	[Rh(COD)H] ₄ ^c	1.83	1.43	
2	[Rh(COD)H] ₄ -SiO ₂	1.59	2.26	
3	[Rh(COD)H] ₄ -SiO ₂ /40 °C	3.33	2.64	
4	[Rh(COD)H] ₄ -SiO ₂ /200 °C	5.13	4.17	
5	[Rh(COD)H] ₄ -Pd-SiO ₂	4.80	4.10	
6	[Rh(COD)H] ₄ -Pd-SiO ₂ /40 °C	3.77	3.03	
7	[Rh(COD)H] ₄ -Pd-SiO ₂ /200 °C	1.07	0.85	
8	[Rh(COD) ₂] ⁺ BF ₄ ^{-c}	0.02	0.02	0.03 (24)
9	[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂	0.02	0.47	0.67 (100)
10	[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /40 °C	1.58	0.99	0.67 (10)
11	[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /200 °C	4.10	3.05	
12	[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂	3.83	3.07	
13	[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /40 °C	3.50	3.11	
14	[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /200 °C	0.76	0.69	
15	[Rh(COD)Cl] ₂ ^c	0.00	0.01	
16	[Rh(COD)Cl] ₂ -SiO ₂	0	0	0.01 (72)
17	[Rh(COD)Cl] ₂ -SiO ₂ /40 °C	0.72	0.75	
18	[Rh(COD)Cl] ₂ -SiO ₂ /200 °C	7.00	5.67	
19	[Rh(COD)Cl] ₂ -Pd-SiO ₂	3.87	3.60	
20	[Rh(COD)Cl] ₂ -Pd-SiO ₂ /40 °C	5.13	3.93	4.00 (24)
21	[Rh(COD)Cl] ₂ -Pd-SiO ₂ /200 °C	0.00	0.60	
22	Rh-SiO ₂	2.52	2.32	
23	Rh-(Pd-SiO ₂)	0.31	0.31	
24	Rh/Pd-SiO ₂	0.52	0.50	0.44 (24)
25	Rh/Pd(O ₂)-SiO ₂	0.03	0.03	0.02 (24)
26	Pd-(Rh-SiO ₂)	0.43	0.37	

^a Reaction conditions: 50 mg (~9.8 μmol Rh) of solid catalyst, 5 ml of toluene, 40.0 °C, 1 atm of H₂ (Eq. (1)).

^b AR: atomic rate is defined as moles of methylcyclohexane produced per total moles of rhodium min (Eq. (2)).

^c 9.2 μmol of homogeneous catalyst.

[Rh(COD)₂]⁺BF₄⁻-SiO₂/200 °C (AR = 4.10 min⁻¹) (entry **11**).

For the catalyst [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂, prepared by adsorbing [Rh(COD)₂]⁺BF₄⁻ onto Pd-SiO₂, an initial activity is observed that is very high (AR = 3.83 min⁻¹) (entry **12**). Hydrogen pretreatments of this catalyst appear to have no beneficial effects. A 40 °C pretreatment produces no appreciable change in rate (AR = 3.50 min⁻¹) (entry **13**). A 200 °C hydrogen pretreatment (entry **14**) severely reduces the catalytic activity by almost five-fold (AR = 0.76 min⁻¹).

3.3. Activities of [Rh(COD)Cl]₂-based catalysts

The activities of [Rh(COD)Cl]₂-based catalysts for the hydrogenation of toluene are given in Table 1. In solution and on silica, [Rh(COD)Cl]₂ shows little ac-

tivity even after 3 days (AR <0.01 min⁻¹) (entries **15** and **16**). However, if the rhodium catalyst on silica is treated with hydrogen gas at elevated temperatures, the system becomes active (entries **17** and **18**). With 1 day of hydrogen pretreatment at 40 °C, the catalyst, [Rh(COD)Cl]₂-SiO₂/40 °C, exhibits a AR of 0.72 min⁻¹. When the system is pretreated at 200 °C for 4 h, a nearly 10-fold rate increase is observed: the initial AR is 7.00 min⁻¹ and the extended AR is 5.67 min⁻¹ after 6 h.

When the same rhodium precursor is adsorbed onto Pd-SiO₂, the catalyst, [Rh(COD)Cl]₂-Pd-SiO₂, is highly active (entry **19**) from the outset (AR = 3.87 min⁻¹). Once again hydrogen pretreatments provide no benefit for rhodium complexes on Pd-SiO₂; pretreatment of [Rh(COD)Cl]₂-Pd-SiO₂ with H₂ at 40 °C has little effect on the activity (AR =

5.13 min⁻¹) (entry **20**), while H₂ pretreatment at 200 °C nearly eliminates the activity (entry **21**) of the catalyst (after 6 h, the rate is only AR = 0.60 min⁻¹).

3.4. Activities of RhCl₃-based catalysts

The rates of hydrogenation of toluene to methylcyclohexane at 40 °C under 1 atm of H₂ catalyzed by catalysts prepared by impregnation with RhCl₃ are summarized in Table 1. The activity (entry **22**) of Rh-SiO₂ is very good (AR = 2.52 min⁻¹). When RhCl₃ and palladium are combined on SiO₂ using several different methods of preparations (see Section 2.2.2), all resulting catalysts are less active than Rh-SiO₂. Impregnation of RhCl₃ onto Pd-SiO₂ gives a catalyst {Rh-(Pd-SiO₂)} with a very low activity (AR = 0.31 min⁻¹) (entry **23**). A catalyst prepared by coimpregnation of rhodium and palladium (Rh/Pd-SiO₂) exhibits a modest activity (AR = 0.52 min⁻¹) (entry **24**), but it is still slower than that of Rh-SiO₂; if in the preparation of this catalyst, the reduction is preceded by a calcination step (Rh/Pd(O₂)-SiO₂), the catalyst is nearly inactive (AR = 0.03 min⁻¹) (entry **25**). Palladium supported on Rh-SiO₂ {Pd-(Rh-SiO₂)} is also dramatically slower (AR = 0.43 min⁻¹) (entry **26**) than the parent Rh-SiO₂.

3.5. Activities of catalysts in the presence of mercury

3.5.1. Toluene hydrogenation

A number of catalysts that are active for toluene hydrogenation were examined for their activities in the presence of mercury metal (Table 2). For all of the catalysts studied, the reactions are quenched completely within 20 min of mercury addition.

3.5.2. 1-Hexene hydrogenations

The [Rh(COD)₂]⁺BF₄⁻ series of catalysts were examined for 1-hexene hydrogenation activity at 0.0 °C both in the absence and presence of mercury (Table 3). In the absence of mercury, [Rh(COD)₂]⁺BF₄⁻ in solution (1 ml CH₂Cl₂:4 ml 1-hexene) and adsorbed on SiO₂, [Rh(COD)₂]⁺BF₄⁻-SiO₂, are very poor hydrogenation catalysts of 1-hexene (AR = 0.0 min⁻¹). The addition of mercury to these systems has no activating effect, AR = 0.0 min⁻¹. In contrast, the hydrogen-pretreated catalysts, [Rh(COD)₂]⁺BF₄⁻-

Table 2

Rates^a of toluene hydrogenation in the presence of mercury^b

Catalyst	AR (1 h)	With Hg ^c
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /40 °C	1.58	0
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /200 °C	4.10	0
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂	3.83	0
[Rh(COD)H] ₄ -SiO ₂ /200 °C	5.13	0
[Rh(COD)H] ₄ -Pd-SiO ₂	4.80	0
Rh-SiO ₂	2.52	0

^a Rates given as AR (mol MeCy/(mol Rh min)) based on total Rh content.

^b Reaction conditions: 40.0 °C, 1 atm H₂, 5.0 ml toluene, and 25 mg (~4.9 μmol Rh) of supported catalyst.

^c Rate after addition of 0.2 ml (14 mmol) Hg.

SiO₂/40 °C and [Rh(COD)₂]⁺BF₄⁻-SiO₂/200 °C, both show similar high activities (AR ~34 min⁻¹). The addition of mercury to these systems results in no immediate change in activity. However, a slow deactivation is apparent. After 2 h of contact time, activity has dropped by a third or more; and after 17 h of mercury exposure, the catalysts are completely deactivated (AR = 0.0 min⁻¹).

The activity of Pd-SiO₂ for 1-hexene hydrogenation, unlike toluene hydrogenation, is comparable to the rhodium complexes on SiO₂. The initial rate for

Table 3

Rates^a of 1-hexene hydrogenation^b

Catalyst	AR ^c	Hg ^d (2 h) ^e	Hg ^d (17 h) ^f
[Rh(COD) ₂] ⁺ BF ₄ ^{-g}	0.0	0.0	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ ^h	0.0	0.0	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /40 °C ^h	34.6	14.5	0.0
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /200 °C ^h	34.0	2.70	0.0
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ ^h	116	14.6	0.0
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /40 °C ^h	160	20.6	0.0
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /200 °C ^h	161	27.3	0.0
Pd-SiO ₂ ⁱ	65.2	1.62	0.0

^a Rates given as AR (mol hexane/(mol Rh min)) based on total Rh content.

^b Reaction conditions: 0.0 °C, 1 atm H₂, 5.0 ml 1-hexene.

^c AR measured over the first 5 min of reaction.

^d 0.2 ml (14 mmol) of Hg added.

^e Rate 2 h after Hg addition.

^f Rate 17 h after Hg addition.

^g 4.0 mg (9.9 μmol Rh) of homogeneous complex in 4.0 ml 1-hexene and 1.0 ml of CH₂Cl₂.

^h 25 mg (~4.9 μmol Rh) of supported catalyst.

ⁱ 25 mg of 10% Pd-SiO₂, rate given as AR_{eff}, see footnote 1.

Pd-SiO₂ is AR_{eff} = 65.2 min⁻¹. Mercury poisoning of supported palladium is slow but more pronounced than for supported rhodium; after 2 h, activity has decreased more than 60-fold (AR_{eff} = 1.62 min⁻¹). After 17 h of contact, mercury exposure completely quenched the hydrogenation ability of Pd-SiO₂ (AR_{eff} = 0.0 min⁻¹)¹.

The catalysts prepared by adsorbing [Rh(COD)₂]⁺BF₄⁻ on Pd-SiO₂ are very active for 1-hexene hydrogenation at 0 °C. Without hydrogen pretreatment, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂ shows an initial activity of 116 min⁻¹. Both pretreated samples, [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C and [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C show similar initial activities (AR ~160 min⁻¹). Addition of mercury to all [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂-based catalysts causes a slow decrease in 1-hexene hydrogenation activity. After 2 h, the activities decrease by a factor of ~8, and complete quenching is observed after 17 h.

3.6. Characterization of catalysts by IR, TEM, and XPS

After exposure to CO, all catalysts showed distinctive ν(CO) bands in their DRIFT spectra. For all of the [Rh(COD)Cl]₂ catalysts, the concentration of rhodium carbonyl species on the surface of the fresh catalysts was too low for DRIFT detection. For all of the catalysts shown in Fig. 3, the catalysts used in a toluene hydrogenation show CO bands that are the same as those observed in the unused catalyst, but the intensities of the bands are reduced. For all the CO-treated catalysts in Fig. 3, no surface rhodium carbonyl species are removed by toluene or CH₂Cl₂ washes, as determined by the absence of IR bands in the washes.

TEM studies of the [Rh(COD)H]₄-SiO₂/40 °C and [Rh(COD)H]₄-SiO₂/200 °C catalysts clearly indicate that rhodium crystallites are present. Visual inspection of the electron micrographs reveals rhodium rafts with a wide range of sizes (Figs. 4 and 5). The nature of these particles is confirmed by micro-chemical analy-

¹ To facilitate comparison, the rates for Pd-SiO₂ catalysts are reported in terms of an effective AR, AR_{eff}. Since these catalysts do not contain rhodium, a AR based on rhodium content cannot be given. The AR_{eff} value is calculated by assuming that the Pd-SiO₂ catalyst contains the standard rhodium loading (9.8 μmol).

Table 4
XPS^a analysis of catalysts

Catalyst	Use ^b	Rh	Pd
		3d _{5/2}	3d _{5/2}
[Rh(COD) ₂] ⁺ BF ₄ ⁻	New	308.6	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂	New	308.4	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /40 °C	New	307.4	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂ /200 °C	New	307.1	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂	0.5 h	307.9	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂	2.0 h	308.3	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -SiO ₂	7.5 h	307.0	–
[Rh(COD)H] ₄	New	308.2	–
[Rh(COD)H] ₄ -SiO ₂	New	308.3	–
[Rh(COD)H] ₄ -SiO ₂ /40 °C	New	307.0	–
[Rh(COD)H] ₄ -SiO ₂ /200 °C	New	307.0	–
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ ^c	New	308.0	335.3
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /40 °C	New	307.3	334.7
[Rh(COD) ₂] ⁺ BF ₄ ⁻ -Pd-SiO ₂ /200 °C	New	306.9	334.9
Rh-SiO ₂	New	307.2	–
Pd-SiO ₂	New	–	334.7

^a For experimental details see Section 2.6. Signals are given in eV.

^b “New” denotes freshly prepared catalysts examined by XPS prior to toluene hydrogenation. Listed times indicate the reaction times that the catalysts were used for toluene hydrogenation under standard reaction conditions (40.0 °C, 1 atm H₂) prior to XPS analysis.

^c See footnote 2.

sis and electron diffraction of the crystallites (Fig. 6). The diffraction patterns (Fig. 6(a) and (b)), are explicit for face centered cubic (fcc) rhodium metal. For example, distances of 2.2 Å are measured for the (1 1 1) plane and 1.9 Å for the (2 0 0) plane, which match the literature values for the distances found in fcc rhodium metal [24].

XPS data obtained from many of the catalysts are collected in Table 4. Further discussion of these data will be presented in Section 4.1.3.

4. Discussion

4.1. Catalyst characterization

4.1.1. IR studies of the catalysts

Although ν(CO) spectra of catalyst samples treated with CO are often useful for identifying species present on the surface, this identification may be complicated by similar ν(CO) spectra of the various species. For supported metallic rhodium, two main species have been identified (Fig. 7). The

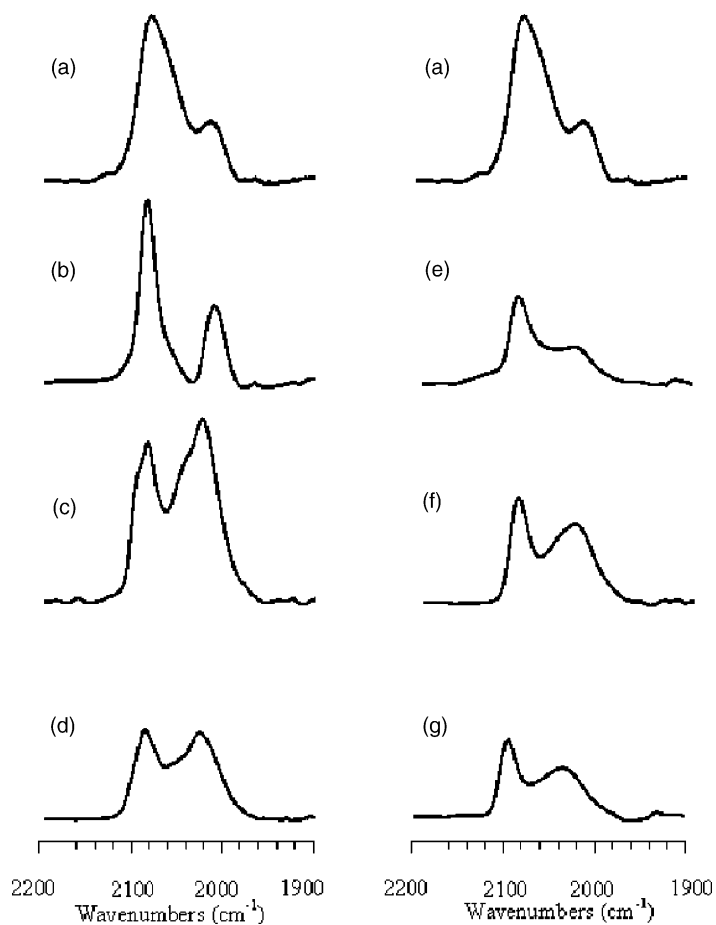


Fig. 3. DRIFT spectra of CO-exposed catalysts: (a) Rh-SiO₂, (b) [Rh(COD)₂]⁺BF₄⁻-SiO₂, (c) [Rh(COD)₂]⁺BF₄⁻-SiO₂/40 °C, (d) [Rh(COD)₂]⁺BF₄⁻-SiO₂/200 °C, (e) [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂, (f) [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C, (g) [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C.

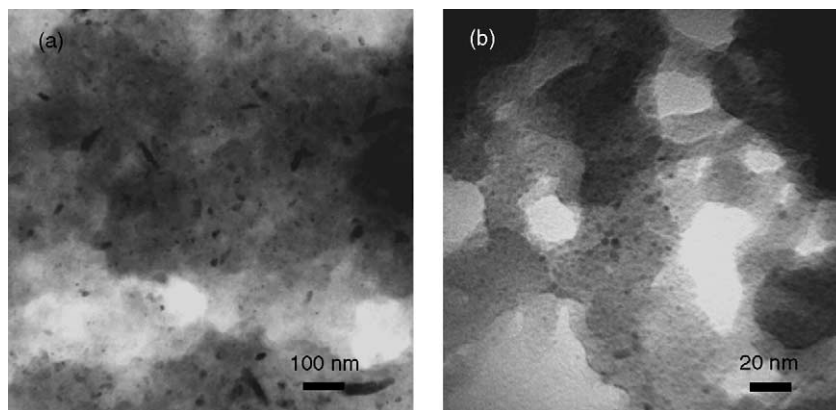


Fig. 4. TEM micrographs of [Rh(COD)H]₄-SiO₂/40 °C (a) and [Rh(COD)H]₄-SiO₂/200 °C (b).

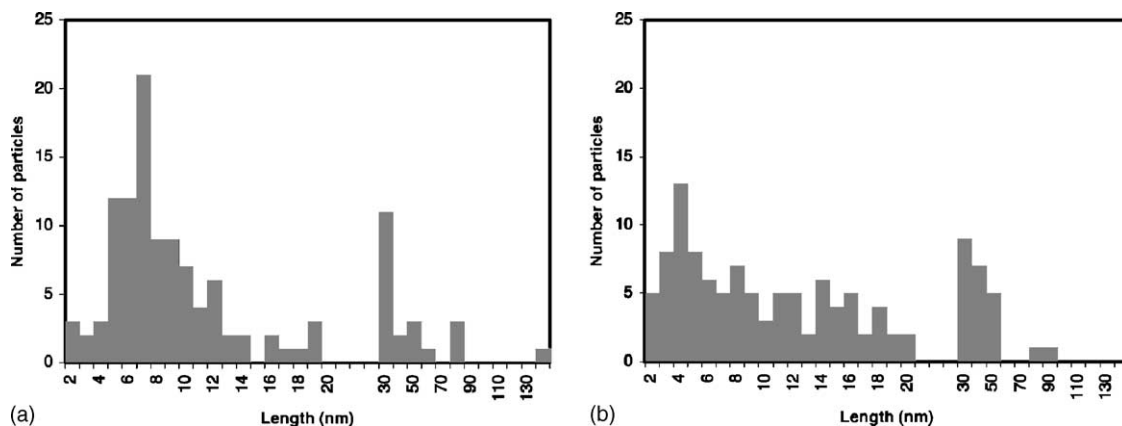


Fig. 5. Size distributions of rhodium crystallites determined by TEM and imaging analyses of $[\text{Rh}(\text{COD})\text{H}]_4\text{-SiO}_2/40^\circ\text{C}$ (a) and $[\text{Rh}(\text{COD})\text{H}]_4\text{-SiO}_2/200^\circ\text{C}$ (b). Note the change in length (nm) scale for particle sizes larger than 20 nm.

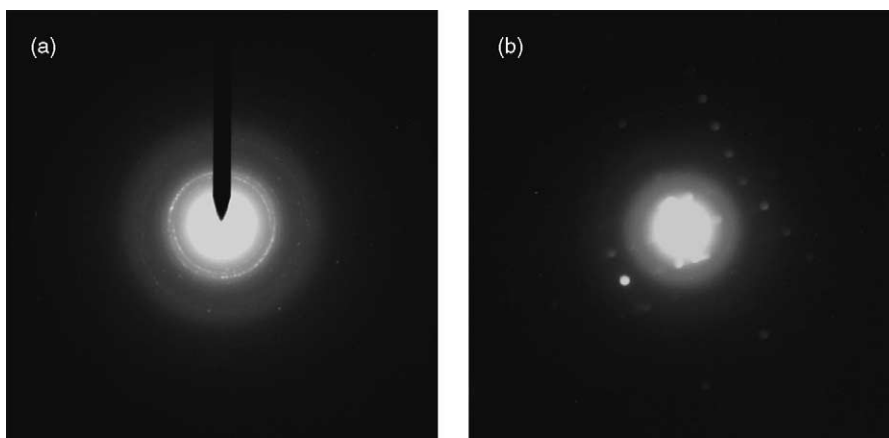


Fig. 6. Electron diffraction patterns of polycrystalline $[\text{Rh}(\text{COD})\text{H}]_4\text{-SiO}_2/40^\circ\text{C}$ (a) and single crystallite $[\text{Rh}(\text{COD})\text{H}]_4\text{-SiO}_2/200^\circ\text{C}$ (b) samples.

rhodium(I) dicarbonyl species, $\text{Rh}^{\text{I}}(\text{CO})_2$, exhibits CO bands at $2096(\text{s})$ and $2038(\text{s})\text{cm}^{-1}$, although the bands are shifted slightly depending on the support [25–32]. The CO linearly bound to bulk islands

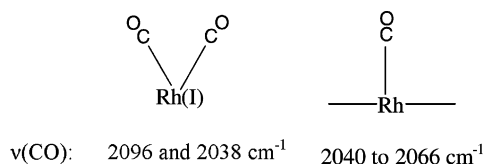


Fig. 7. Reported CO-containing species on Rh-SiO₂.

of rhodium metal show a coverage dependent signal, which ranges from 2040 (at low coverages) to 2066cm^{-1} (at high coverages) [25,26]. The situation is further complicated by the possible formation of several surface-constrained homogenous species such as $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{Cl}(\text{H}_2\text{O})]$, and even $\text{Rh}(\text{CO})_x$ that are known to exhibit IR bands similar to those of surface bound rhodium dicarbonyl or linearly bound CO on rhodium metal [33,34].

For the catalysts in this work, the $\nu(\text{CO})$ signals may be interpreted to indicate the presence of surface bound $\text{Rh}^{\text{I}}(\text{CO})_2$ species and adsorbed CO on bulk rhodium (Fig. 3). All of the CO-containing

rhodium complexes on the surface are strongly bound to the silica surface as toluene and CH_2Cl_2 extractions fail to yield solutions containing species with $\nu(\text{CO})$ bands. Thus, soluble complexes such as $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}(\text{CO})_2\text{Cl}(\text{H}_2\text{O})]$, or $\text{Rh}(\text{CO})_x$, which are known to be readily soluble in pentane, toluene, or CH_2Cl_2 and easily washed from silica surfaces [33,34], are not present or formed upon CO adsorption.

Attempts to characterize rhodium sites on the CO-treated catalysts, by correlating catalyst activity with specific $\nu(\text{CO})$ bands gave no consistent correlations. Unused Rh-SiO₂ (Fig. 3, trace a) shows the characteristic Rh^I(CO)₂ bands (2092(vs) and 2027(m) cm⁻¹). $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂ (Fig. 3, trace b) and $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂ (Fig. 3, trace e) show very similar IR signatures (2089(vs) and 2030(m) cm⁻¹). For $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ on SiO₂ and Pd-SiO₂, a CO band at 2055 cm⁻¹ appears as a shoulder with hydrogen pretreatments (Fig. 3, traces c, d, f and g). Also, for the hydrogen-treated catalysts containing $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ on SiO₂ and Pd-SiO₂, the relative intensities of the 2089 and 2030 cm⁻¹ bands are changed from those of the untreated catalysts (Fig. 3, traces b and e). These changes may be due to the appearance of rhodium metal clusters. However, the similarities of these spectra to those of the samples that had not been hydrogen-treated complicate interpretation. Thus, the observed DRIFTS of hydrogen-pretreated samples may result from signals from both residual starting complex (with a large extinction coefficient) and CO on metallic rhodium. Similar results were obtained from DRIFT studies of $[\text{Rh}(\text{COD})\text{H}]_4$ on SiO₂ and Pd-SiO₂ (not shown).

4.1.2. TEM studies of the catalysts

For $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂/40 °C and $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂/200 °C, TEM micrographs (Fig. 4) and electron diffraction patterns (Fig. 6) clearly show the presence of rhodium crystallites, which suggests that the active species is supported rhodium metal. The mean size (9.8 nm) of the rhodium particles of the $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂/200 °C sample is slightly smaller than those (13.8 nm) of the $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂/40 °C sample (Fig. 5). Thus, dispersion may play a vital role in the greater activity of the 200 °C hydrogen pretreated sample; smaller particles will have more

surface area, more active sites, and therefore higher observed activity.

4.1.3. XPS analyses

4.1.3.1. $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$. For the series of catalysts containing $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ on SiO₂, distinct Rh 3d_{5/2} signals are observed (Table 4). The solid complex $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ exhibits a signal at 308.6 eV, which corresponds well to literature values for Rh(I) complexes (~308 eV) [35]. The $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂ catalyst exhibits a very similar signal at 308.4 eV; this is both diagnostic for Rh(I) and suggests that the $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ complex remains intact. Thus, the initial adsorbed complex is still Rh(I) prior to pretreatment with hydrogen and/or use in hydrogenation reactions. After hydrogen pretreatment, the Rh 3d_{5/2} signals for $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂/40 °C (307.4 eV) and $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂/200 °C (307.1 eV) are in the correct range for Rh(0) (307 eV) [35] and match well with Rh-SiO₂ (307.2 eV).

When the catalyst $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂ is examined after 30 min of toluene hydrogenation, the main Rh peak is seen at 307.9 eV. Even after 2 h of reaction, the Rh signal is at 308.3 eV. These signals indicate the presence of Rh(I) and reflect the poor activity of the $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂ catalyst during the induction period, which continues for at least 6 h. After 7.5 h of reaction, the Rh peak has clearly shifted to 307.0 eV, in the correct range for Rh(0) metal, and the catalyst is nearly fully active.

4.1.3.2. $[\text{Rh}(\text{COD})\text{H}]_4$. For the $[\text{Rh}(\text{COD})\text{H}]_4$ complex (Table 4), the XPS signal is at 308.2 eV. For the $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂ catalyst, the signal (308.3 eV) suggests the presence of Rh(I). After hydrogen pretreatments, however, the Rh signal indicates the presence of Rh(0): $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂/40 °C (307.0 eV) and $[\text{Rh}(\text{COD})\text{H}]_4$ -SiO₂/200 °C (307.0 eV). This result directly confirms the TEM results, in Section 4.1.2.

4.1.3.3. $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂. The XPS spectra of $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ on Pd-SiO₂ are similar to those on SiO₂ (Table 4). For the untreated $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂ catalyst, the Rh signals are virtually the same as those of the untreated $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂: Rh at 308.0 eV and Pd at

335.3 eV.² Hydrogen pretreatments had a discernable effect on the Rh signal but almost no effect on the Pd signal; compare $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂/40 °C (Rh at 307.3 eV and Pd at 334.7 eV) and $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂/200 °C (Rh at 306.9 eV and Pd at 334.9 eV). This indicates that, as for $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂, the complex is reduced to Rh(0) only after hydrogen pretreatment or reaction.

4.2. Mercury poisoning experiments

The ability of mercury to poison heterogeneous metal catalysts, but not homogenous metal catalysts, is documented in the literature [36,37]. The observation that mercury completely quenches toluene hydrogenation (Table 2) supports the conclusion that metallic rhodium is the active catalyst. Similarly, 1-hexene hydrogenation activity (Table 3) is quenched by mercury. The observation that $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ in solution and $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂ without pretreatment are inactive for 1-hexene hydrogenation, together with the XPS results (Table 4), demonstrates that the active catalyst for both 1-hexene and toluene hydrogenation is metallic rhodium.

4.3. 1-Hexene hydrogenation rates

It is interesting to compare the initial 1-hexene hydrogenation activity of the catalysts formed from $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ on SiO₂ and on Pd-SiO₂. In particular, 40 and 200 °C hydrogen-pretreated catalysts on the same support have similar 1-hexene hydrogenation activities (Table 3). The rates for $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂/40 °C (AR = 34.6 min⁻¹) and $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂/200 °C (AR = 34.0 min⁻¹) suggest that the same number of rhodium sites are present on both 40 and 200 °C pretreated catalysts. Also, the overall rates for $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂/40 °C (AR = 160 min⁻¹) and $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂/200 °C (AR = 161 min⁻¹) suggest approximately the same number of rhodium sites for these two catalysts, assuming the palladium on both catalysts contributes

the same amount to the overall rate. Finally, the absence of 1-hexene hydrogenation activity with $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -SiO₂ (AR = 0.0 min⁻¹) in contrast to the substantial activity of $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂ (AR = 116 min⁻¹)³ points to a facile reduction of the rhodium complex to metallic rhodium in the presence of palladium and H₂, even at 0 °C.

4.4. General activity trends

Several general trends in toluene hydrogenation activity are the same for catalysts prepared from all of the rhodium precursors ($[\text{Rh}(\text{COD})\text{H}]_4$, $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$, and $[\text{Rh}(\text{COD})\text{Cl}]_2$). On silica, the adsorbed species (entries 2, 9 and 16 in Table 1) start out no more active than they are in solution (entries 1, 8 and 15), but over time the adsorbed catalysts either come close or out-perform the solution species. The activities of the catalysts (entries 2, 9 and 16) are improved by hydrogen pretreatments prior to reaction. The activity increases with the temperature of the hydrogen pretreatment, 200 °C (entries 4, 11 and 18) being better than 40 °C (entries 3, 10 and 17). For rhodium catalysts on Pd-SiO₂ (entries 5, 12 and 19), a different trend is observed. The catalysts (entries 5, 12 and 19) are more active from the outset and show higher activities than the same metal complex on SiO₂ (entries 2, 9 and 16). Furthermore, on Pd-SiO₂, the higher temperature (200 °C) pretreatment reduces the activity of the catalyst (entries 7, 14 and 21). For these catalysts on Pd-SiO₂ (entries 5, 12 and 19), the untreated catalyst is the most active of the series, and hydrogen pretreatments do not have a beneficial effect.

Although there are pronounced differences in toluene hydrogenation activity of the rhodium complexes in solution ($[\text{Rh}(\text{COD})\text{H}]_4 \gg [\text{Rh}(\text{COD})_2]^+\text{BF}_4^- > [\text{Rh}(\text{COD})\text{Cl}]_2$), their activities are similar when adsorbed on SiO₂ and treated with H₂ at 200 °C (entries 4, 11 and 18). In addition, all of the adsorbed rhodium complexes on Pd-SiO₂ have comparable activities (entries 5, 12 and 19). Also, the catalysts pretreated at 200 °C on SiO₂ (entries 4, 11 and 18)

² Additional $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂ catalysts were examined with different Rh:Pd loadings. For Rh:Pd (w/w) ratios of 2:10, 2:5, 2:2.5, and 2:1, the XPS spectra were all the same, consistent with Rh(I) (~308 eV) and Pd(0) (~335 eV) [35].

³ Note that the activity of $[\text{Rh}(\text{COD})_2]^+\text{BF}_4^-$ -Pd-SiO₂ is not solely due to the Pd in the system as the observed AR (116 min⁻¹) is well above that for Pd-SiO₂ alone (AR_{eff} = 65.2 min⁻¹ [footnote 1]).

and those on Pd-SiO₂ (entries **5**, **12** and **19**) all have similar activities (AR ~4 min⁻¹) regardless of the rhodium precursor. The one exception is the unusually active [Rh(COD)Cl]₂-SiO₂/200 °C (**18**); perhaps the very low loading (Rh, 0.093 wt.%) of rhodium in this case leads to much greater rhodium dispersion and thus higher observed activity per total rhodium content.

Finally, it is instructive to consider the catalysts prepared by impregnation with RhCl₃·H₂O (Table 1, entries **22–26**). The only catalyst prepared from RhCl₃·3H₂O with good activity is the standard rhodium on silica, Rh-SiO₂ (entry **22**). Any catalyst that is prepared from both RhCl₃·3H₂O and PdCl₂ has substantially lower activity no matter which metal is introduced first or even if they are coimpregnated (entries **23–26**). One common aspect of these catalysts and similar rhodium-palladium bimetallic examples in the literature [7,8] is that their preparations involve a high temperature (>200 °C) reduction step with hydrogen. Also, the adsorbed catalysts ([Rh(COD)H]₄, [Rh(COD)₂]⁺BF₄⁻, and [Rh(COD)Cl]₂) on Pd-SiO₂ (entries **5**, **12** and **19**), that are pretreated at 200 °C with hydrogen have relatively low activities (entries **7**, **14** and **21**).

4.5. Interpretation of hydrogenation activity

All methods of characterization (DRIFTS, TEM, XPS, and mercury poisoning experiments) suggest that the toluene hydrogenation activity of these rhodium-containing catalysts is due to the formation of rhodium metal. This metal formation could occur by reduction pathways similar to those proposed for the reduction of Rh nanoparticles on supports [23] or in solution [38]. The conclusion that the active catalyst is rhodium metal is supported by the observation that the activities of the bimetallic systems ([Rh(COD)H]₄, [Rh(COD)₂]⁺BF₄⁻, and [Rh(COD)Cl]₂ on Pd-SiO₂) are very similar to that of reduced rhodium on silica (Rh-SiO₂) in the absence of palladium (compare entries **5** and **4**; **12** and **11**; **19** and **18**). The similar activities of [Rh]-Pd-SiO₂ and [Rh]-SiO₂/200 °C, where [Rh] is [Rh(COD)H]₄, [Rh(COD)₂]⁺BF₄⁻, and [Rh(COD)Cl]₂, suggest that both contain similar amounts of reduced rhodium species. The effect of the palladium in the [Rh]-Pd-SiO₂ systems is to facilitate the reduction of the Rh complex to active rhodium

metal species. Perhaps, the palladium reduces the rhodium precursors to rhodium metal by providing highly active spillover hydrogen [6]. It is interesting to note that the process is very quick and effective, as no induction period is observed (less than 5 min), and it is equivalent to 4 h of hydrogen pretreatment at 200 °C. Furthermore, the resulting Rh-Pd-SiO₂ catalysts are more active than those of the same composition prepared by classical impregnation methods [7,8]. The scope, utility, and mechanism of the palladium assisted reduction requires further investigation.

Toluene hydrogenation activities of the [Rh]-Pd-SiO₂ catalysts are reduced by high temperature (200 °C) pretreatment with hydrogen (entries **7**, **14** and **21**, as well as **23–26**). For example, the 200 °C pretreatment reduced the toluene hydrogenation activity of [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C (AR = 3.50 min⁻¹) to [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C (AR = 0.76 min⁻¹). This treatment apparently changes the structure of the catalyst perhaps to a form similar to that of other bimetallic rhodium-palladium catalysts supported on silica or alumina, which are substantially less active for arene hydrogenation than just rhodium on the same supports [7,8]. This lower activity was attributed either to the formation of a rhodium-palladium alloy or to the formation of rhodium clusters that are smaller than the 10 Å size required for this activity. In contrast to the structure sensitivity of toluene hydrogenation, 1-hexene hydrogenation rates are the same for both [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/40 °C (AR = 160 min⁻¹) and [Rh(COD)₂]⁺BF₄⁻-Pd-SiO₂/200 °C (AR = 161 min⁻¹). This observation is consistent with the structure-insensitive nature of supported rhodium-palladium catalysts reported for other alkene hydrogenation reactions [8].

5. Conclusions

In conclusion, the adsorption of homogenous rhodium complexes ([Rh(COD)H]₄, [Rh(COD)₂]⁺BF₄⁻, and [Rh(COD)Cl]₂) onto silica produces catalysts that are more active than those (Rh-SiO₂) produced by the standard incipient wetness method utilizing RhCl₃·H₂O. The most active of these, those pretreated with hydrogen at 200 °C or adsorbed onto Pd-SiO₂, are nearly twice as active

as Rh-SiO₂. In addition, the use of Pd-SiO₂ as a support for rhodium complexes gives catalysts that have no induction period. Such induction periods in the [Rh]-SiO₂ catalyst can also be eliminated by pretreatment of the catalysts at 200 °C under H₂. The only real difference in catalytic behavior among the three rhodium precursors is their rate of reduction to rhodium metal: [Rh(COD)H]₄ > [Rh(COD)₂]⁺BF₄⁻ > [Rh(COD)Cl]₂. Finally, it is shown for [Rh]-SiO₂ catalysts that Rh(0) is the active catalytic species for toluene and 1-hexene hydrogenation. For [Rh]-Pd-SiO₂, Rh(0) is the active toluene hydrogenation catalyst, while both palladium and rhodium metal are responsible for 1-hexene hydrogenation activity. The [Rh]-Pd-SiO₂ catalysts that were not pretreated with hydrogen exhibit toluene hydrogenation activities that are greater than other Rh-Pd bimetallic catalysts in the literature [7,8].

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