Reactivity of mesoporous palladium yttria-stabilized zirconia for solution phase reactions

Carl Poulin, Matthew A. Brown, Yamile A. Wasslen, Catherine M. Grgicak, Keith Fagnou, and Javier B. Giorgi

Abstract: A reduced mesoporous 5% Pd-YSZ precatalyst was observed to be very active for the Heck reaction providing up to 770,000 TON. Three-phase tests have experimentally confirmed that a leached homogeneous species is responsible for the activity. Residual Pd concentration in solution is minimal (<0.10 ppm) and therefore this material has potential applications because it can be easily removed by filtration. This paper describes the synthesis, structural characterization, and catalytic activity of the mesoporous Pd-YSZ material. The material was prepared using an amphiphilic surfactant templating method resulting in a homogeneous dispersion of Pd in an ordered mesoporous structure. Material properties were fully characterized using X-ray diffraction, surface area analysis, and electron microscopy.

Key words: mesoporous catalysts, palladium, yttria-stabilized zirconia, Heck reaction, Pd-YSZ.

Introduction

Palladium-catalyzed transformations have become widespread in the construction of new carbon–carbon and carbon–heteroatom bonds (1–5). Recent advances in the development of new homogeneous palladium catalysts have enabled these transformations to be carried out even with very deactivated substrates such as aryl chlorides under mild conditions (6). In the context of product purity, however, the use of homogeneous catalysts has drawbacks including the fact that the palladium must be removed from the organic product at the end of the reaction (7, 8). This can sometimes be very challenging and costly. With this challenge in mind, chemists have been studying the use of heterogeneous palladium catalyst systems as viable alternatives to the more intensively studied homogeneous catalysts (9). In recent years, a variety of heterogeneous supports have appeared including carbon, silicates, zeolites, and block copolymers (10–16). Alternatively, homogeneous catalysts have been “heterogenized” via immobilization of active homogeneous catalysts on various solid supports (17–26). With all of these heterogeneous catalysts, however, there is debate with respect to the true nature of the active catalyst (27). Some catalysts do appear to function as true heterogeneous catalysts (28, 29), while others have been shown to be catalyst reservoirs (precatalysts) from which an active catalyst leaches into solution (28, 30–38). Analysis of these reactions is further complicated by a third option in which a release and capture mechanism involving catalyst leaching and subsequent readsorption onto the matrix support occurs upon reaction completion. Since the question of catalyst form is of paramount importance, more studies are warranted in this area, particularly when new catalysts and (or) supports are being designed and studied. Simple coupling reactions such as Heck or Suzuki can be used as the standard to test catalyst performance of heterogeneous catalysts.

In the design of heterogeneous catalysts, maximization of the active surface area is the key to performance together with the nature of the catalytic species. Metal catalysts such as palladium have been shown to be in their most active state when speciated as nanoparticles (39). In this state, a maximum of palladium sites are exposed while the catalytic properties are controlled by the electronic structure of the...
nanoparticle and influenced by its support. The optimization of the active surface area was revolutionized with the discovery of mesoporous structures, which provide a maximum total surface area with channels of the appropriate size for reactant transport (40–42). Examples of the improved performance of mesoporous silica-based catalysts date back to their petrochemical origins (43) and enhanced properties continue to surface, as recently demonstrated for ethane hydrogenolysis and ethylene hydrogenation (44), hydrogenation of phenyl acetylene (45), and anti-stokes luminescence of encapsulated dyes (46). A particularly appropriate example has recently used mercaptopropyl modified silica to anchor Pd atoms to the SBA-15 zeolitic framework (16). The modified zeolite is an excellent Pd scavenger and has been used successfully as a Pd catalyst for low-turnover high-yield coupling reactions with minimal Pd leaching.

A considerable effort has been made over the past 15 years to obtain mesoporous metal oxide materials that possess enhanced properties in catalysis, charge transport, and host–guest affinities. Since the family of silicate mesoporous molecular sieves was first synthesized (40–42), efforts have been made toward the synthesis of mesoporous transition metal oxide materials (47–50) and, in particular, mesoporous yttria and zirconia materials have been recently developed (51–53). The general synthetic methodology to prepare mesoporous oxides uses an amphiphilic surfactant as a template. In solution, the surfactant agglomerates into micelles and the inorganic oxide framework grows around it. Upon removal of the organic species, the resulting precipitate is filtered, washed, and dried. This “as-synthesized” (dried) material consists of the micellar CTAB array around which the Pd-YSZ matrix has been formed. Upon calcination, the organic component is eliminated giving rise to the porous structure (Fig. 1).

Details of the procedure are as follows. Zirconium ethoxide (5.0 g, Strem Chemicals Inc., 99.9+%) and 2.4 equiv. of NaOH (1.8 g) were added to a flask containing excess ethylene glycol (51 mL, spectroscopic grade, Sigma-Aldrich Chemical Ltd.). The resulting mixture was then refluxed at 180 °C under flowing nitrogen for 24 h. Excess ethylene glycol was distilled off leaving a thick yellowish gel (zirconium glycolate). Separately, yttrium glycolate was prepared by adding yttrium acetate tetrahydrate (1.2 g, Alfa Aesar, 99.9%) to ethylene glycol (31 mL) and stirring. The zirconium and yttrium glycolates were then added to a polypropylene bottle containing a Pd(NO3)2 source (2.0 mL solution 10 wt% in stabilized zirconia (YSZ) with mesoporous structure (54–56).

In this paper, we report the synthesis and characterization of a versatile palladium catalyst supported on a mesoporous yttria-stabilized zirconia (YSZ) framework. These materials, which are characterized by a high surface area, have the potential to be used in a liquid–solid regime for the catalysis of organic reactions (57, 58), which has been validated by demonstrating high turn-over numbers in the Heck reaction. Catalyst structure along with reaction kinetics and mechanisms are discussed.

**Experimental**

**Pd-YSZ preparation**

The general synthesis involves the formation of yttrium and zirconium glycolates separately by reaction of ZrCl4(OEt)3 with ethylene glycol. The solutions are combined and a Pd(NO3)2 source is added in appropriate proportion according to the desired loading. Cetyltrimethylammonium bromide (CTAB) is added as a template to form the mesoporous structure. The solution is allowed to age and finally the resulting precipitate is filtered, washed, and dried. This “as-synthesized” (dried) material consists of the micellar CTAB array around which the Pd-YSZ matrix has been formed. Upon calcination, the organic component is eliminated giving rise to the porous structure (Fig. 1).

Details of the procedure are as follows. Zirconium ethoxide (5.0 g, Strem Chemicals Inc., 99.9+%) and 2.4 equiv. of NaOH (1.8 g) were added to a flask containing excess ethylene glycol (51 mL, spectroscopic grade, Sigma-Aldrich Chemical Ltd.). The resulting mixture was then refluxed at 180 °C under flowing nitrogen for 24 h. Excess ethylene glycol was distilled off leaving a thick yellowish gel (zirconium glycolate). Separately, yttrium glycolate was prepared by adding yttrium acetate tetrahydrate (1.2 g, Alfa Aesar, 99.9%) to ethylene glycol (31 mL) and stirring. The zirconium and yttrium glycolates were then mixed in a dropwise fashion while the zirconium glycolate was still hot (~50 °C). The resulting solution was added to a polypropylene bottle containing a Pd(NO3)2 source (2.0 mL solution 10 wt% in...
10 wt% nitric acid), cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich Chemical Ltd., 4.1 g), NaOH (1.7 g), and water (120 mL). The mixtures were stirred at RT for 25 min and then put into an oven for 5 days at 80 °C. The solid products obtained were collected by vacuum filtration and washed two times with water to remove residual chlorine and CTAB. Samples were then dried at 120 °C for 6 h and denoted as-synthesized. This procedure produces a Pd loading of 5%; for different loading the Pd concentration is simply adjusted.

Calcination to 600 °C or 950 °C was performed in air for 2 h to ensure the crystallization of the YSZ. The calcination procedure also produces PdO. When reduced Pd is required, reduction was performed at 500 °C under H₂ flow for 2 h for samples previously calcined to 600 °C, and at 800 °C under N₂ flow for 2 h for samples previously calcined to 950 °C. A reduced material containing 5 mol% Pd and calcined to 950 °C prior to reduction shall be denoted as 5%Pd-YSZ950 and one precalcined to 600 °C as 5%Pd-YSZ600.

Pd-YSZ characterization

Powder composition and crystallite sizes were determined by X-ray diffraction (XRD) (Phillips PW1830) using Cu Kα radiation with a wavelength of 1.54 Å. Crystalline phases were assigned using the Powder Diffraction File database (ICCD, 2001). The crystallite size analysis of each phase was performed using the Williamson–Hall methodology, which takes into account crystallite strain (59). Vibrational characterization of the powders prior to calcination was determined using Attenuated Total Reflection Fourier transform IR spectroscopy (ATR-FTIR) (Bruker Equinox 55). The BET surface area of the calcined powders were determined using the Kelvin equation.

General procedure for the Heck reaction of butylacrylate with iodobenzene

To a round-bottomed flask fitted with a reflux condenser was added iodobenzene (4.0 mmol, 0.45 mL), butylacrylate (4.8 mmol, 0.69 mL), N,N-diisopropylethylamine (DIPEA) (8 mmol, 1.4 mL), and N,N-dimethylformamide (DMF) (1.4 mL). To this solution was added the precatalyst 5% Pd-YSZ (0.004 mmol, 9.7 mg). The reaction was then heated to 140 °C. Reaction progress was monitored by GC-MS analysis of the crude reaction mixture against a decane internal standard. For all reactions, the mol ratio iodobenzene–butylacrylate–DIPEA was kept at 1:1:2.2.

Triple phase test

Preparation of resin

To a mixture of Wang resin (0.3 equiv.) and iodobenzene (1 equiv.) in DMF (0.1 mol/L) was added dicyclohexyl-carbodiimide (1 equiv.) and a few grains of 4-dimethylaminopyridine as catalyst. The reaction mixture was heated at 60 °C for 4 days. The solution was filtered and washed twice with each of the following solvents: water, methanol, dichloromethane (DCM), and diethyl ether.

Capping of the unreacted hydroxyls on the resin

To a suspension of the resin (1 equiv.) in dichloromethane (0.1 mol/L) was added acetic anhydride (5 equiv.) and pyridine (5 equiv.). The reaction was stirred for 24 h at RT. The reaction mixture was filtered and washed twice with each of the following solvents: water, methanol, DCM, and ether to afford the acetyl protected resin.

Reaction and cleavage of compound from the resin

To a mixture of acetate protected resin (1 equiv.) was added butyl acrylate (3 equiv.), DIPEA (3 equiv.), Pd-YSZ (0.05 equiv.) in DMF (0.16 mol/L). The reaction mixture was heated at 130 °C for 3 h. The resin (1 equiv.) was filtered and washed thoroughly before being stirred in a 1:1 mixture of trifluoroacetic acid and dichloromethane (0.5 mol/L) for 2 h. The resulting mixture was filtered and washed twice with each of the following solvents: methanol, DCM, and ether. The filtrate was put under reduced pressure at 70 °C to remove the volatiles as well as the trifluoroacetic acid. This afforded compound 5 (eq. [1]).

Thiol scavenger test

To a suspension of thiol resin (0.5 equiv.) was added iodobenzene (1 equiv.), butyl acrylate (1.2 equiv.), DIPEA (2 equiv.), and Pd-YSZ (0.01 equiv.) in DMF (2.7 mol/L). The reaction mixture was heated to 130 °C and monitored by GC. After prolonged reaction time, no greater than 2% conversion was detected.

Results and discussion

Pd-YSZ material properties

The as-synthesized material containing the residual hydrocarbon micelles possesses long-range order with d-spacing of 40 Å, as seen by the low-angle peak in the XRD pattern (Fig. 2). Upon calcination in air to 600 °C, the hydrocarbon is eliminated leaving a porous mesostructure with d-spacing of 41 Å. The low-angle peak is decreased in intensity, consistent with a partial disruption of the long-range order. The observed change in d-spacing is consistent with a thickening of the pore walls as the crystals of YSZ become larger (56).
Finally, upon calcination to 950 °C the material is described as having lost its long-range order.

The shape of the low-angle peak for the as-synthesized material is observed as very broad and asymmetrical. Such a shape has been observed by Ozin and coworkers (54–56) in similar materials and discussed in terms of a poor long-range order of the mesoporous structure. An alternative explanation is the superposition of two peaks for different orientations of the long-range order structure (53). Kim et al. (53) assigned their peak at 2θ = 3.9° to the (110) reflection of a hexagonal arrangement of meso-zirconyl chloride. In this case, the metastable structure present when the surfactant is still in the pores is disturbed when the organic component is removed, leaving a single peak in the XRD pattern of the calcined samples.

The mesoporous structure of the material calcined to 600 °C is also reflected by the intermediate surface area, typically in the range of 150 m² g⁻¹, and a slightly asymmetric pore size distribution that peaks at 19 Å in diameter with an average pore size diameter of 26 Å, as calculated by the Kelvin equation. This value is smaller than those obtained for perfectly structured mesoporous materials such as zeolites, but it is an order of magnitude larger than most commercial YSZ catalyst powders (Maketech Materials 70% NiO/8YSZ, 9.8 m² g⁻¹ and 34% NiO/8YSZ, 6.63 m² g⁻¹). The surface area decreases to ~10 m² g⁻¹ upon calcination to 950 °C indicating the predominant collapse of the porous structure.

Removal of the pore-forming molecule CTAB from the material is achieved during the calcination process and is complete by 600 °C. This is illustrated in Fig. 3, which shows ATR-FTIR spectra of a sample as-synthesized and after calcination. The two peaks present at 2850 and 2916 cm⁻¹ in the as-synthesized sample are characteristic of the C–H stretching modes in the CTAB long chain. These peaks are removed upon calcination. The regions around 1500 and 3400 cm⁻¹ are characteristic of water and can be seen to decrease substantially upon calcination. Peaks at ~1000 cm⁻¹ are associated with yttrium and (or) zirconium species, but their identification is difficult due to the large broadening (60).

It is interesting to note that the CTAB species are not removed at a single temperature and in fact they appear to be partially decomposed and trapped within the porous structure. Thermogravimetric analysis in helium shows weight loss at several distinct temperatures (Fig. 4). Correlation of the weight loss with mass analysis shows that in the temperature range below 60 °C, water is the main component desorbed. The hydrocarbon moieties represented by the ethyl group (mle = 29) are desorbed in the subsequent two peaks at 280 and 440 °C. Trapping and decomposition of the CTAB is suggested by the simultaneous observation of zirconium (mle = 91) and the tertiary amine group (mle = 57), which come out from the matrix at 440 °C. These observations have direct implications on the stability of the mesoporous structure. The binding and (or) trapping of CTAB to the YSZ network is sufficiently strong that the removal of the surfactant disrupts the pores. A more inert surfactant may improve the thermal stability of the YSZ porous structure.

Palladium and YSZ crystallites are present in the material as individual phases as seen from their characteristic powder diffraction pattern. The large width of their peaks suggests extremely small crystallite sizes, particularly for YSZ. Increasing the calcination temperature results in an increase in size of the YSZ crystallites, as observed by a decrease in peak widths in the XRD patterns (Fig. 5).

During the calcination process, the crystallites of palladium originally present (Fig. 5) also increase in size. However, as the temperature rises Pd is oxidized to PdO. At a temperature of 840 °C, PdO is reduced to Pd once again. The reduction of PdO to Pd can be readily observed in the TGA experiment performed in air as a sharp decrease in mass (Fig. 6). It is interesting to note that the reoxidation of Pd to PdO during cooling occurs more gradually around 650 °C, a hysteresis of 190 °C. The observed temperature of PdO reduction in air is high for zirconia-based catalysts, but it is consistent with literature (61–63) for other Pd-oxide catalysts. The ratio of oxidized vs. metallic palladium observed in the XRD (at RT, after calcination to 950 °C, Fig. 5) depends on the sample cooling rate in air. Calcination to
600 °C in air produces only the PdO phase. To obtain metallic Pd exclusively, the samples can be calcined and cooled in an inert atmosphere.

Palladium sintering effects in heterogeneous catalysis are a general concern for temperature treatments above 800 °C because coarsening leads to a decrease in catalytic activity (61–63). In these mesoporous Pd-YSZ materials, palladium crystallites remain constant in size up to 800 °C during the oxidation and subsequent reduction process. Calcination to higher temperatures does increase the Pd crystallite size, but only to a limited extent (Table 1). The ultimate average crystallite size upon calcination depends on the palladium content with a maximum coarsening of three-fold observed for 20% Pd loading. The observed increase in crystallite size compares very well to increases of over 10-fold for Pd-Al2O3 (64, 65) and nanoengineered 3%Pd-YSZ (66) catalysts at similar temperatures. For all samples, the YSZ average crystallite size after calcination to 950 °C is around 20 nm, regardless of Pd loading. The relatively stable mesostructure of the YSZ, which partially survives the calcination process, seems to be responsible for the low degree of sintering of palladium. Figure 7 shows an SEM image of 5%Pd-YSZ950R (reduced palladium) where the homogeneous nature and the small particle size of the material can be assessed.

Application to the Heck Reaction

A 5 mol% material with the highest possible surface area was chosen for catalytic experiments. The mesoporous 5 mol% Pd-YSZ framework possesses long-range order with a d-spacing of 40 Å (by XRD). Crystallites sizes of 10 nm and 5 nm for Pd and YSZ respectively were measured for samples calcined to 600 °C. This highly reactive 5%Pd-YSZ600R has a total surface area of 150 m²/g with an average pore size diameter of 26 Å. For comparison, a 5% Pd loading material calcinated to 950 °C in the reduced form was chosen (5%Pd-YSZ950R). Higher temperatures during the material preparation process disrupt the long-range order of the mesoporous structure and lead to the overall reduction of surface area to 10 m²/g. However, up to 1000 °C the increase in the crystallite size of the two components is relatively small, ~2×. Generally, catalytic materials with smaller total surface areas are not expected to perform as well under reaction conditions. However, for selected reactions the
high-temperature treatment may be preferred because it adds mechanical, chemical, and thermal stability to the catalysts, which have a direct impact on the reusability of the catalysts. Preliminary work showed that both of these precatalysts were active for the Heck reaction, even prior to the reduction step. The subsequent sections compare the performance of these two precatalysts and provide a discussion of their effectiveness and the reaction mechanism involved for a standard Heck coupling reaction.

**Reaction optimization**

With an active catalyst in hand, the reaction conditions were optimized with respect to solvent, base, temperature, and concentration. In early screens, dimethylformamide (DMF) emerged as the optimal solvent. A base scan also revealed that the best outcomes were achieved with organic bases such as diisopropylethylamine (DIPEA). Inorganic bases such as potassium bicarbonate lead to lower turnover numbers (TONs) and slower reaction. All subsequent optimization studies were performed in DMF with DIPEA as base.

Initial optimization reactions were performed with 5%Pd-YSZ950R (reduced Pd). From three experiments performed at 120, 130, and 140 °C, it was determined that faster reactions and improved TONs were achieved at 140 °C. For example, after 60 min of reaction time less than 10% conversion was observed at 120 °C compared with 47% and 65% conversion at 130 and 140 °C, respectively (Table 2, entries 1–3).

These reactions are very sensitive to concentration as illustrated in Table 2, entries 4–7. Four different iodobenzene concentrations were assayed (0.2, 0.5, 1.0, and 1.2 mol/L) and each of the reactions was analyzed after 30 min. At these intervals, neither reaction at 0.2 and 0.5 mol/L showed any conversion to product. On the other hand, reactions performed at 1.0 and 1.2 mol/L had progressed to 35% and 75% conversion after 30 min, respectively, showing that a faster initial reaction occurs at elevated concentration. It is interesting to note that in Table 2, entries 4–7, the substrate to catalyst ratio (S/C) is kept constant and therefore the effect of concentration is different from the homeopathic effect described by de Vries (27) where a large S/C ratio prevents Pd nucleation and subsequent deactivation of the catalytic species.

A comparison of the two precatalysts 5%Pd-YSZ950R and 5%Pd-YSZ600R was carried out. From these experiments (Table 2, entries 8–11), the 5%Pd-YSZ600R emerges as a superior catalyst as evidenced by the percentage conversion at 30 min (Table 2, entry 10 vs. 8) and 60 min (Table 2, entry 11 vs. 9). With these conditions in hand, reactions were performed to determine the maximal TON that could be achieved with this new catalyst. We were delighted to see that under optimal conditions, up to 770,000 TON could be achieved after approximately 7 days (Table 2, entry 12).

**Elucidation of the active species**

With an active catalyst in hand, we were interested in determining unequivocally if this was a heterogeneous catalyst or if palladium was leaching off of the support to produce an active homogeneous species. Two different approaches were taken to answer this question based on the three-phase test concept (67–70). In the first case, the aryl halide was anchored to a Wang resin (71). If the true catalyst in these processes was purely heterogeneous then interaction between the supported substrate and the matrix bound catalyst should not be possible, thus preventing reaction. In contrast, if palladium leaching occurs and if this soluble palladium species is catalytically active, then Heck reaction at the solid-supported should be observed. When supported was reacted under standard conditions followed by separation of the solid phase, washing of the Wang resin, and cleavage of the substrate-product mixture from the solid support via treatment with trifluoroacetic acid in dichloromethane (72, 73), approximately 50% conversion to was observed (eq. [1]). This lends strong support to the notion that a homogeneous active catalyst is generated under the reaction conditions via leaching from the YSZ support.

![Fig. 7. Scanning electron micrograph of 5%Pd-YSZ950. Image is taken with an r-filter for improved contrast. High palladium concentration areas appear brighter, although Pd is homogeneously distributed in this sample as confirmed by energy dispersion measurements.](image-url)
To determine if an active heterogeneous catalyst species was also contributing to the direct arylation reaction, another three-phase test was conducted. In this experiment 1 was reacted under standard conditions in the presence of a silica supported thiol-based scavenger resin. Since thiols are known to have a very high affinity for palladium, the presence of this heterogeneous metal scavenger should sequester the homogeneous catalyst as it is produced. On the other hand, a heterogeneous palladium species that is catalytically active should not be poisoned by the presence of the heterogeneous metal scavenger. After 16 h, less than 5% of the desired product had been formed while an identical reaction run in parallel without the scavenger resin reached 100% conversion (eq. [2]). This indicates that the heterogeneous palladium is not catalytically active on the timescale examined and that the observed reactivity arises from the in situ generation of a homogeneous catalyst.

Table 2. Heck reaction optimization.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Substrate–Catalyst Ratio</th>
<th>Temp (°C)</th>
<th>Conc. [B]</th>
<th>Reaction Time (min)</th>
<th>% Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>100</td>
<td>140</td>
<td>0.2</td>
<td>60</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>100</td>
<td>130</td>
<td>0.2</td>
<td>60</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>100</td>
<td>120</td>
<td>0.2</td>
<td>60</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>100</td>
<td>140</td>
<td>0.2</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>1000</td>
<td>140</td>
<td>0.5</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>1000</td>
<td>140</td>
<td>1.0</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>A</td>
<td>1000</td>
<td>140</td>
<td>1.2</td>
<td>30</td>
<td>75</td>
</tr>
<tr>
<td>8</td>
<td>A</td>
<td>1000</td>
<td>130</td>
<td>0.5</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>9</td>
<td>A</td>
<td>1000</td>
<td>130</td>
<td>0.5</td>
<td>60</td>
<td>49</td>
</tr>
<tr>
<td>10</td>
<td>B</td>
<td>1000</td>
<td>130</td>
<td>0.5</td>
<td>30</td>
<td>41</td>
</tr>
<tr>
<td>11</td>
<td>B</td>
<td>1000</td>
<td>130</td>
<td>0.5</td>
<td>60</td>
<td>61</td>
</tr>
<tr>
<td>12</td>
<td>B</td>
<td>1000000</td>
<td>140</td>
<td>1.0</td>
<td>7 days</td>
<td>77</td>
</tr>
</tbody>
</table>

Note: Catalyst A: 5%Pd-YSZ950R and B: 5%Pd-YSZ600R. Conditions: Iodobenzene, butylacrylate, N,N-diisopropylethylamine (DIPEA), and N,N-dimethylformamide (DMF) added to a round-bottomed flask followed by the addition of the catalyst and heating to the indicated temperature.

*Concentration of iodobenzene.

To determine if an active heterogeneous catalyst species was also contributing to the direct arylation reaction, another three-phase test was conducted. In this experiment 1 was reacted under standard conditions in the presence of a silica supported thiol-based scavenger resin. Since thiols are known to have a very high affinity for palladium, the presence of this heterogeneous metal scavenger should sequester the homogeneous catalyst as it is produced. On the other hand, a heterogeneous palladium species that is catalytically active should not be poisoned by the presence of the heterogeneous metal scavenger. After 16 h, less than 5% of the desired product had been formed while an identical reaction run in parallel without the scavenger resin reached 100% conversion (eq. [2]). This indicates that the heterogeneous palladium is not catalytically active on the timescale examined and that the observed reactivity arises from the in situ generation of a homogeneous catalyst.

Having shown that the mechanism of reaction is homogeneous, we investigated how much Pd is lost during the process. As it was not possible to identify Pd in solution, we determined the amount of palladium before and after reaction to obtain an upper limit to the amount of palladium remaining in solution after reaction. Figure 8 shows the XRD pattern of catalysts 5%Pd-YSZ950R before and after undergoing a reaction. XRD was chosen to search for PdO, which could have been formed during reaction, but was not observed. Although XRD is not a traditional quantitative technique, we can clearly see that the ratio of Pd to YSZ has decreased substantially. Since YSZ is not affected by the reaction, it can be considered as an internal standard for the XRD measurement allowing us to use the intensity ratio of the variable (Pd) to the standard (YSZ) for quantization purposes. A quantitative value can be obtained by measuring the intensity ratio of the most intense peaks for Pd and YSZ (at 40 and 30 °, respectively) and comparing this to a calibration curve obtained for variable amounts of Pd in YSZ. The technique cannot measure atomic Pd in the sample, but after a sintering treatment to allow palladium aggregation, no change was observed. If we consider that all the Pd not present in crystalline form in our sample has remained in solution, we obtain an upper limit to the amount of Pd leached. Estimating that about 80% of the Pd was lost during reac-

Fig. 8. Powder XRD pattern of 5%Pd-YSZ950. Diffractograms have been normalized to the peak at 2θ = 30° (the most intense YSZ peak) for (a) before undergoing reaction and (b) after undergoing reaction.
tion, this would correspond to ~0.10 ppm of Pd in the final solution (e.g., Table 2, entry 12). This value is consistent with best effort for Pd on activated carbon (0.05 ppm) and only slightly worse than the mercaptopropyl-modified silica (0.003 ppm), which is a Pd scavenger (16).

Structure–reactivity analysis

The activity of different precatalysts can be analyzed in terms of total number of turn-overs and how fast that TON can be achieved, namely kinetics. In fact, the optimization of reaction parameters will be most sensitive to the kinetics of reaction. For these reasons, we chose the lower surface area catalyst, which we expected would be slower, to optimize the other reaction parameters. Table 2 (entries 1–9) shows a subset of the reaction optimization data for the Heck reaction using 5%Pd-YSZ950R.

Our previous work demonstrated that if reactions were allowed sufficient time (24 h), the conversion for 100:1 (substrate–catalyst) reactions was >95% for a wide range of conditions. Therefore, the difference in reactivity for the two catalysts was assessed by comparison of the percentage conversion vs. time for different catalysts and conditions. For example, entries 8–11 in Table 2 for a substrate–catalyst ratio of 1000:1 show that after 0.5 h of reaction 5%Pd-YSZ600R has a TON 3x higher than 5%Pd-YSZ950R. This result is consistent with the heterogeneous catalysis literature since more active catalyst is usually exposed in higher surface area materials. In this case, because of the homogeneous nature of the reaction mechanism the higher surface area and smaller Pd particle size of 5%Pd-YSZ600R facilitate the extraction of Pd to solution, thereby making the reaction faster.

However, the support seems to be playing a more important role than simply controlling the surface area of available palladium. It is interesting to note that the activity of the catalyst is also reflected in the total number of turn-overs. 5%Pd-YSZ600R attains 770,000 turn-overs after 7 days, approximately twice as much as 5%Pd-YSZ950R. This effect may be accounted for by the mesoporous structure of 5%Pd-YSZ600R, which may be preventing the active homogeneous Pd species from diffusing into the bulk of the solution (encapsulation) where it can be easily de-activated (27).

Despite the homogeneous nature of the catalysts due to leaching of Pd into solution, 5%Pd-YSZ600R compares well with other heterogeneous precatalysts discussed in the literature. While TONs for homogeneously catalyzed Heck reactions have been documented in excess of 8.0 × 10^6 (75), TONs with heterogenous precatalysts are typically much lower. In rare cases, TONs in slight excess of 10^6 have been obtained demonstrating that the Pd-YSZ catalytic examined in these studies compares favourably with other catalyst systems. The highest value we have found in the literature is slightly higher (TON 1,150,000 (29, 76)) for a complex polymer-based ligand-coordinated palladium catalyst. In contrast, palladium supported on activated carbon, with similar cost per gram of catalyst as our precatalyst, has been shown to achieve TONs of 36,000 (74, 77).

Conclusions

Pd-YSZ has been prepared using an amphiphilic surfactant templating method resulting in a homogeneous dispersion of Pd on an ordered mesoporous structure. The Pd particle size and composition properties are easily controllable. The material is resistant to high temperatures, although some coarsening is observed and the long-range order is maintained only up to intermediate temperatures.

Reduced Pd-YSZ showed high activity for the Heck reaction. Up to 770,000 TON were achieved with a 5% Pd-loaded catalyst having a surface area of 150 m^2/g. This result compares favourably with other heterogeneous precatalysts in this reaction. Three-phase tests were conducted to ascertain the nature of the active catalyst species. These tests revealed that a homogeneous catalyst is leaching from the solid support and that the palladium that remains on the matrix is not responsible for the observed reactivity. Despite the homogeneous nature of the active species, the heterogeneous precatalyst remains interesting because it can be easily filtered out leaving behind only residual amounts of Pd (<0.10 ppm).

Acknowledgments

The authors thankfully acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the contribution of the Center for Catalysis Research and Innovation at the University of Ottawa.

References
