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PdAlqEn: A Novel Upgraded Version of the PdEnCat[™] Family of Polyurea Encapsulated Catalysts

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Abstract: Palladium nanoparticles are stabilized and encapsulated in a combination of polyurea and an ionic liquid (Aliquat 336) to obtain the PdAlqEn hybrid catalyst. The novel composite material is applied as a recyclable and robust catalyst in hydrogenation reactions.

Keywords: Aliquat 336; hydrogenation; microencapsulation; PdAlqEn catalyst; PdEnCatTM; polyurea

Microencapsulation is one of the most promising techniques for catalyst immobilization. The group of commercial catalysts based on palladium(II) acetate entrapped in a polyurea (PU) matrix, reported by Ley and co-workers^[1] (marketed under the trade name PdEnCatTM), has been described as versatile, active, robust and recycleable catalyst. These catalysts were successfully applied in various cross-coupling C-C bond forming reactions such as the Suzuki, Stille and the Heck reactions. Some of the latter processes were carried out in supercritical CO₂ as solvent and were also demonstrated in a laboratory scale continuous flow system. In an alternative version, the encapsulated catalyst was reduced to Pd(0) nanoparticles and this hybrid catalyst showed activity in hydrogenation and hydrogen transfer reactions. Only a negligable amount of catalyst leaching to solution was reported in these reactions.

The robustness and recyclability, as well as the mode of action of the PdEnCatTM were recently challenged in two independent studies using different experimental methodologies. Broadwater and McQuade^[2] utilized the "three-phase" test to assess the activity of PdEnCat in the Suzuki coupling and the Heck reactions where one of the substrates (aryliodide) was covalently attached to a resin. The latter polymeric substrate could obviously react only when a soluble catalyst is present in the system. Testing three different commercial PdEnCat catalysts, the au-

thors verified that swift catalytic reaction took place with the resin bound aryl iodide unquestionably substantiating that a sufficient amount of active catalyst leached out of the polymeric matrix under the reaction conditions. An even stronger argument was put forward by Richardson and Jones^[3] who tested PdEn-Cat40TM in the Heck reaction where specific polymeric palladium catalyst poisons, namely poly(4-vinylpyridine) and Quadrapure TU (a polymer-bound thiourea derivative) were added to the reaction mixtures under various conditions. These polymers inhibit only soluble catalytic species and cannot affect the encapsulated catalyst. Since no reaction could be detected in the presence of each of these resins it was unequivocally concluded that the polyurea encapsulated palladium is inactive in the Heck reaction and that the observed activity was a result of palladium leaching to the solution.

We have now examined $Pd(0)EnCat30^{TM}$ (purchased from Aldrich) as catalyst in the simple hydrogenation reaction of 4-phenyl-3-butene-2-one to 4phenyl-2-butanone [(Eq. (1)] at 70 °C in toluene and



in methanol under 1 bar hydrogen pressure. A smooth hydrogenation reaction was realized (GC analysis) with a complete conversion of the substrate after 40 min with 100%. The measured TOF was 0.027 sec^{-1} . Upon addition of poly(4-vinylpyridine) or Quadrapure TU to the reaction mixture (poisons that inhibit soluble catalyst only) the hydrogenation rate fell to 30% of its original level. This clearly suggests that, similar to the observations made in the Heck and Suzuki reactions, the major part of the catalytic activity in this system is taking place in solution and not within the polyurea microcapsules.

Examining particles of the PdEnCatTM catalyst by energy dispersive X-ray spectroscopy (EDS) com-

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Figure 1. Morphology of Pd(0)EnCat30TM. *Left*, fresh catalyst (×400); *middle and right*, after hydrogenation reaction of Eq. (1) (×200) (×1000).

bined with scanning electron micrography (SEM) in backscattered mode, before and after the catalytic process, revealed that a dramatic change in the manifestation of the polyurea spheres is taking place in the course of the reaction. This is shown in Figure 1 where Pd(0)EnCat30 is exposed prior to the hydrogenation reaction (*left*, magnification $\times 400$) and after filtration and separation from the hydrogenation mixture (*middle*, magnification × 200 and *right*, magnification $\times 1000$). It is evident that the spherical capsules are cracked and fractured during the reaction and that the palladium particles (appearing as white stains) are exposed to the exterior. XPS analyses revealed that the surface mass concentration of Pd on the original catalyst particles was 4.7% while on the surface of the catalyst recovered from the hydrogenation reaction the surface mass concentration of Pd tripled to 11.2%. Our immediate conclusion was that the polyurea matrix utilized for the fabrication of the PdEnCatTM is not robust and stable as originally claimed and that the material breaks down almost instantly upon exposure to the very mild catalytic conditions.

We alleged that the main drawback of the PdEnCat stems from the interfacial encapsulation process which evidently creates a weak and fragile shell with low porosity and small surface area.^[4] Assessing that the latter is a result of excess of surface active agents remaining in the particles' crust, we have removed all the three emulsifiers and dispersing agents advocated by Ley et al. and replaced them with a single reagent – tricaprylmethylammonium chloride (Aliquat 336) which, as will be shortly described, not only served as effective emulsifier in the encapsulation process but also played a critical and multidimensional role in the preparation and performance of the immobilized catalyst.

In addition, in view of the recent critical reviews by Jones,^[5] by DeVries^[6] and by Finke^[7] we inferred that

the actual catalyst in all the reactions where PdEnCat was used is Pd(0) and not Pd(II). Consequently we have deliberately reduced (using sodium borohydride) the palladium(II) to stabilized Pd(0) nanoparticles concurrently with the interfacial polymerization.

Using the protocol described below in the Experimental Section we have prepared a novel version of the polyurea encapsulated Pd(0) catalyst which we entitle PdAlqEn. The latter was characterized to have average particle diameter of 4 μ m and high surface area (BET 1.50 m²g) (compared, respectively, to 250 μ m and 0.07 m²g for PdEnCat30TM). The porosity of PdAlqEn was determined to be 5.45 mm³g. TEM analysis of the polyurea matrix showed evenly distributed palladium nanoparticles with a uniform diameter of 2 nm. The palladium content was found to be 0.15 mmol/g of catalyst by ICP analysis.

PdAlqEn was tested in the reaction of Eq. (1) and was confirmed to perform better than the PdEnCat catalyst, achieving complete conversion after 10 min under identical reaction conditions (TOF = 0.11 sec^{-1}). The performance of our catalyst was actually similar to that of 10% Pd/C catalyst containing the same number of Pd atoms. PdAlqEn could be simply and swiftly filtered from the reaction mixture and recycled to a new hydrogenation reaction of Eq. (1) without any apparent loss in catalytic activity even after five consecutive cycles (Figure 2).

Moreover, SEM analysis of PdAlqEn before and after reaction (Figure 3), in methanol or toluene as solvents, revealed that the catalyst is stable under the reaction conditions and its physical appearance and morphology do not change at all even after five consecutive runs in hydrogenation of 4-pheynl-3-buten-2one [Eq. (1)]. No change in the initial surface concentration of Pd (0.05%) was monitored after the reaction, based on XPS analysis.

Only a negligible decline (1-3%) in the catalytic activity of PdAlqEn in the reaction of Eq. (1) was ob-



Figure 2. PdAlqEn catalyst recycle experiments in the reaction of Eq. (1).

served when either of the poisons PVP, Quadrapure TU or elemental mercury^[8] was added to the reacting mixture. This clearly suggests that the catalytic activity is limited to the bulk of the polymeric matrix and no part of the catalyst is active in solution.

The crucial component in the new proposed formulation of polyurea microencapsulation is the quaternary ammonium salt, Aliquat 336^[9] which is also an ionic liquid. We explain the unique multifunctional role of this ingredient as follows.

(i) A surface active agent^[10] that supports the formation of water/toluene emulsion in which the interfacial polymerization is performed. We have measured a dramatic decrease in the interfacial water/toluene pressure in the presence of Aliquat 336.

(ii) A phase-transfer vehicle that initially extracts $PdCl_4^-$ ions^[11] and in the second step extracts BH_4^-

ions^[12] and H₂O molecules^[13] into the oil phase (see Experimental Section). We perceived that the presence of both BH_4^- and water in the organic phase is essential for the rapid conversion of the isocyanate function into amine thus allowing the polymerization to take place. In the absence of either Aliquat 336 or of borohydride the polymerization is very sluggish and ineffective.

(iii) The Aliquat 336-promoted tandem extraction of $PdCl_4^-$ and of BH_4^- leads to rapid reduction of the Pd(II) species to Pd(0) nanoparticles. The lipophilic ammonium salt then stabilizes^[14] the palladium nanoparticles in the polyurea matrix. NMR analysis, elementary analysis and mass balance calculations confirmed that the Aliquat 336 completely remains within the polymeric matrix after the preparation and after several consecutive catalytic runs.

For further understanding of the nature of palladium metal and its distribution in the matrix of PdAlqEn, we carried out a transmission electron microscopy (TEM) study (Figure 4, A) and energy dispersive X-ray spectroscopy (EDAX) coupled with scanning tunneling electron microscopy (STEM) (Figure 4, B). These analyses identified the presence of the palladium metal, the nature of the nanoparticles and the average particle size as 2 nm and also revealed the uniform distribution of palladium nanoparticles within the polymer matrix.

Moreover, the analysis by TEM and by electron diffraction showed a 1D fringe with a *d* spacing of about 0.23 nm (Figure 4, C). Since the common structure of Pd metal is cubic close packed with the unit cell parameter equal to 0.389 nm and *d* spacing equal to 2.24 Å corresponding to the crystal plane,^[1e] this result confirms the effective reduction of the initial palladium(II) to palladium(0). Further, we visualize the microstructure of the catalyst as an array of Ali-



Figure 3. Morphology of PdAlqEn catalyst. *Left*, fresh catalyst (\times 9316); *right*, filtered and dried catalyst after five consecutive hydrogenation runs [Eq. (1)] (\times 9600).



Figure 4. (A) TEM image of PdAlqEn shows the uniform distribution of palladium nanoparticles of 2 nm. (B) STEM image shows the uniform distribution of palladium in the spherical microcapsule. White dots represent the palladium nanoparticles. (C) TEM image through electron diffraction reveal the fundamental state of palladium [Pd(0)].

quat 336 (actually an ionic liquid) globules evenly scattered within the polyurea matrix containing the immobile (thus stabilized) Pd particles (Figure 4, C). The matrix is permeable to the substrates and the products but impassable to the Aliquat/Pd complex.

PdAlqEn was successfully tested in several hydrogenation and hydrogenolysis reactions. Typical examples are shown below [(Eq. (2) and Eq. (3)]. In all





these examples no leaching of metal was detected and the catalyst could be recycled five times without any apparent loss in activity.

To understand the recycle efficiency of catalyst and palladium loss in the reaction of Eq. (2), under identical reaction conditions, a 100% yield of aniline was obtained from the first cycle to the fifth cycle and also we found no loss of palladium from the matrix, which was confirmed by ICP analysis of the catalyst after every cycle. To substantiate this observation further, the reaction solution (filtrate after removal of catalyst) was subjected to the same reaction by the addition of a second batch of substrate (nitrobenzene). We found that no reaction took place under these conditions, which undoubtedly further confirm that there is no palladium leaching from the polyurea matrix. The same observation was seen in the reaction of Eq. (3). Other transition metals such as cobalt, ruthenium, rhodium and gold could be similarly encapsulated as stabilized nanoparticles in polyurea matrix. Their application as catalysts will be published separately.

In conclusion, we have demonstrated that polyurea resin combined with ionic liquid (Aliquat 336) is an excellent and robust support for catalytic nanoparticles of palladium and other transition metals.

Experimental Section

Synthesis of PdAlqEn Ccatalyst

Aliquat 336 (0.5 g, 1 mmol) and 5 g of toluene were mixed in a 50-mL flask. To this solution 0.07 g (0.25 mmol) of Na₂PdCl₄ was added and the mixture was stirred at 50 °C for 10 min. Then 1.2 g (5 mmol) of PMDI were added to the above solution which was stirred for 5 min. This mixture was slowly added to 100 g (5.5 mol) of water containing 0.05 g (1 mmol) of sodium borohydride. Instant and rapid polymerization was observed and stirring was continued for 2 h using an overhead mechanical stirrer at 200 rpm at room temperature. The resulting microcapsules were filtered through a polyethylene frit (20 micron porosity), washed by de-ionized water and by dichloromethane and dried at 100 °C for 4 h to obtain the PdAlqEn(0) catalyst, a brown solid powder.

Representative Procedure for Hydrogenation of Nitroaromatics using PdAlqEn Catalyst

Toluene (5 g) was charged in a round-bottom flask and 1 mmol of substrate and 100 mg (0.015 mmol Pd content) of catalyst were added and heated to 70 °C in a preheated oil bath under stirring. Hydrogen was bubbled in to the mixture through a tube which was connected to a hydrogen cylinder. After stirring the whole mixture for 20 min, a small sample was removed, diluted with dichloromethane and injected in a gas chromatograph [HP 5890 GC, a 95%-dimethyl-5%-diphenyl packed column (25 m length and 0.53 mm ID)]. The GC injection program was: initial temperature 90 °C, (1 min), ramp at 15 °C/min, final temperature 280 °C (5 min). Helium was used as carrier gas at a pressure of

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50 kPa. The GC was calibrated using biphenyl as internal standard. The yields of the products were calculated based on the area percent of the products and confirmed by injecting authentic samples.

For the recycle study, prior to each cycle, the catalyst was separated from the reaction mixture by filtration using Whatman 40 and washed with an excess amount of water and acetone and dried at 100 °C for 2 h. The obtained catalyst was subjected to SEM and ICP analyses to confirm the catalyst morphology and concentration of palladium subsequently used for next cycle.

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