Colloid Polym Sci (2004) 282: 613–619
DOI 10.1007/s00396-003-0986-y

ORIGINAL CONTRIBUTION

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Polymer-protected palladium nanoparticles. Morphologies and catalytic selectivities

Received: 30 April 2003
Accepted: 7 August 2003

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Abstract Colloidal palladium nanocatalysts prepared by in situ reductions of palladium chloride were immobilized and protected by either of two water-soluble polymers. The particle sizes and size distributions of the palladium colloids were determined by transmission electron microscopy. Their selectivities as catalysts were determined by comparing the extents of hydrogenation of carefully chosen pairs of small-molecule olefins. There was found to be high hydrogenation selectivity with regard to cyclic vs. noncyclic olefins. Selectivity was relatively low, however, among olefins that differed only in size (such as hexene vs. octene), or olefins differing only with regard to the positions of the double bonds (such as 1-octene vs. 3-octene). Selectivity could be improved by careful choice of the immobilizing polymer, and by its use at relatively high concentrations.

Keywords Metal nanoparticles · Palladium · Polymer-modified catalysts · Olefin hydrogenation · Catalysis efficiency · Catalysis selectivity

Introduction

Transition metals are useful as catalysts for various chemical reactions, and are often used in the form of metal particles dispersed in a support matrix. Colloidal dispersions of such zero-valent transition metal particles, immobilized and protected by polymers, have received increased attention since such catalyst-polymer systems can exhibit some important advantages over traditional catalysts [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. These advantages include:

- Large surface areas of the metal particles, particularly when in the nanometer size range
- Stabilization of the nanoparticles by suppression of aggregation, and protection from deactivation by oxygen or water vapor
- Possible control of particle shape, porosity, or surface area by varying the nature of the polymer, its molecular weight, degree of branching, cross-link density, etc
- Maintenance of catalytic activity by choice of relatively inert polymers
- Improvement of catalytic selectivity, from the polymer layers on the metal particles

Polymers chosen for such modification of nanocatalysts should fulfill some, or possibly all, of the following requirements:

- Solubility in convenient solvents, and stability at the temperatures required in the syntheses
- Good “protective function” for metal-particle stabilization
- Strong interactions with the metal particles (complex ion-pair formation, etc), for enhanced catalytic selectivity

In many cases, water-soluble polymers have been chosen to immobilize and protect the particles. The synthetic methods involve reduction of the metal ion to the colloidal metal within the polymer medium, followed by coalescence of the polymer onto the nanoparticles formed. A specific example is the preparation of palladium particles by reduction of a salt through the redox reaction oxidizing an alcohol to an aldehyde [1, 2, 3, 4, 23]:

$$PdCl_2+C_2H_5OH \rightarrow Pd + 2HCl + CH_3CHO \qquad (1)$$

This approach uses a water/ethanol medium containing a water-soluble stabilizing polymer, with refluxing under an inert gas. It can produce a homogeneous dispersion of ultrafine particles having diameters 1–5 nm, with a relatively narrow size distribution. Another synthetic possibility is the direct photoreduction of the same salt [7, 8]:

$$PdCl_2 \rightarrow Pd + Cl_2 \qquad (2)$$

Both approaches can yield metal colloids that are stable at room temperature for months. The polymer surrounding the active sites can frequently provide catalytic selectivity through steric or electrostatic interactions with the reactants, or by simple control of their diffusion through the coating. This selectivity in yielding preferred products would be in addition to the advantages of high catalytic activity from the nanoparticle sizes and the long-term stabilities obtained from the protective functioning of the polymer. For example, poly(*n*-vinylpyrrolidone) is thought to have selective interactions with various crystallographic planes of metals such as silver and gold [24, 25] through coordination bonding involving the O and N atoms of the pyrrolidone ring. These selective interactions affect the growth rate of specific crystal planes, with associated effects on particle surface structure, shape, and morphology. This is important since different crystal planes have different catalytic activities; for example, atoms in the {111} plane are less active than those in other planes [4]. Such changes in crystallographic structure may thus change possibilities for coordination with certain substrates, and thus lead to changes in selectivity.

Examples of modifications of catalytic selectivity include use of polymer-immobilized metal complexes (metal-*containing* polymers), various hydrogenations of olefins [1, 5, 26, 27, 28, 29, 30, 31], palladium complexes for the carbonylation of olefins [32], and platinum and rhodium complexes for the hydrosilylation of alkenes [33, 34]. However, selectivity results for polymer-immobilized colloids of zero-valent transition metals are unfortunately limited. An example would be the catalytic selectivity reported for polymer-immobilized palladium colloids in partial hydrogenation of diene to monoene molecules [9], or for immobilized rhodium particles in hydrogenation reactions [35].

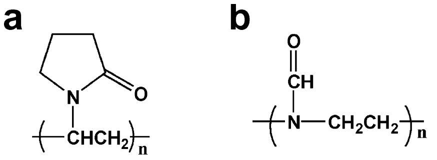

Fig. 1a, b Structures of the immobilizing polymers. **a** poly(*n*-vinylpyrrolidone) (PVPr) and **b** poly(2-ethyl-2-oxazoline) (PEOX)

The present investigation explores the substrate selectivity of several polymer-immobilized palladium metal colloids in the hydrogenation of various small olefins. The immobilizing polymers were poly (*n*- vinylpyrrolidone) (PVPr) and poly(2-ethyl-2-oxazoline) (PEOX), which have often been used to immobilize metal nanoparticles [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. The morphologies of such polymer-immobilized colloidal catalysts were investigated by transmission electron microscopy. Catalytic efficiencies and selectivities were gauged by hydrogenation reactions on pairs of molecules differing in the nature of their unsaturation.

Experimental

Preparation of the colloidal catalysts

Palladium chloride, palladium acetate (PdAc) [$Pd(CH_3COO)_2$], PVPr, and PEOX were purchased from Aldrich. The structural formulae of the polymers are given in Fig. 1. The colloidal palladium catalysts were prepared following the method of Hirai et al. [1, 10], with all glassware being cleaned with aqua regia before use. Specifically, the palladium precursors $PdCl_2$ or PdAc were reduced by refluxing their alcoholic solutions. Compositions were 6.8×10^{-4} M (ethanol:water = 1:1 v/v) and the mass ratios of polymer-to-metal (P/M) being 40:1, and 80:1, as summarized in Table 1. The reflux time was 30 min at an oil bath temperature of 110 °C.

Characterization

The progress of the reduction reaction was followed by UV-Vis spectroscopy from 300 to 600 nm, using a Hewlett Packard 8453 UV-Vis instrument with a quartz cuvette having a 10 mm path length. Relevant here was the disappearance of the absorption

Table 1 Preparative information

Polymer-immobilized catalyst, sample no	Precursor	Immobilizing polymer, M_w (g/mol)	Polymer/metal mass ratios
1	$PdCl_2$	PVPr, 55 000	40/1
2	$PdCl_2$	–	80/1
3	$PdCl_2$	PEOX, 50 000	40/1
4	$PdCl_2$	PEOX, 200 000	40/1

bands for the $PdCl_2$ precursor, located at approximately 320 and 425 nm. Completion of the reaction was evidenced by a simple continuous absorption spectrum in the visible range, which is typical for nanosized palladium colloids [36]. Typical results are shown elsewhere [37].

Transmission electron microscopy (TEM) was used to determine particle sizes, size distributions, and morphologies. The samples were prepared by placing a drop of the colloidal solutions on form-var carbon-coated copper grids and then evaporating the solvent at room temperature. TEM images were obtained with a JEOL-100 CXII instrument, operated at an accelerating voltage of 80 kV, and at least four images were taken for each sample. The size distributions were constructed based on visual measurements of at least 150 particles.

Hydrogenation

The selectivities of the catalysts were investigated by hydrogenations of pairs of selected small olefins. The reaction mixtures contained 0.1 mL of each olefin, 10 mL methyl alcohol, and the desired amount of the catalyst as a colloidal dispersion. The amount of catalyst chosen was 0.24 mg (4 mL of colloidal solution) for 0.2 mL of the olefins. The hydrogenations were carried out in a Parr hydrogenator (shaker type) at 30 psi, for 1 hour at room temperature. The resulting reaction mixtures were analyzed by gas chromatography (DB-5 column), with a flame ionization detector (FID), using nitrogen as the carrier gas. Hydrogenation reactions and reaction mixture analyses were repeated at least three times for each catalyst.

Results and discussion

Electron microscopy results

The particle sizes obtained were found to be strongly dependent on the reduction method and reaction conditions chosen, for example, on the specific reducing agents, metal precursors, and immobilizing polymers. The TEM results revealed primary and secondary structures in the polymer-immobilized catalysts, in agreement with small-angle and ultrasmall-angle X-ray scattering data collected for both the colloidal solutions and solid-film samples [37].

Increase in the polymer/metal ratio had considerable effects on the formation of aggregates and agglomerates (clustered aggregates). Figure 2 shows the (diameter) size distribution and a TEM image for sample 1 (described in Table 1). This material consisted of a palladium colloid immobilized by PVPr having a weight-average molecular weight $M_w \sim 55\,000$ g/mol, with a P/M ratio of 40:1. The most prevalent particle diameters were 4.5, 6.3, and 7.2 nm, and diameters for the smallest and the largest separate particles detected were 2.7 and 10.8 nm. The particles that were well separated are seen to be approximately spherical. There were also many aggregates, however, composed of four or more discernible particles in string-like arrangements and a few clusters composed of at least twelve or more particles.

Catalyst sample 2 with a P/M ratio 80:1, had most-prevalent particle sizes of 6.3 and 9.0 nm, as seen in Fig. 3. The smallest size observed was 2.7 nm. The palladium particles were all well separated and there were virtually no string-like aggregates. It is possible that at higher polymer concentrations, an increased amount of polymer surrounding a particle suppressed the formation of both aggregates and agglomerates.

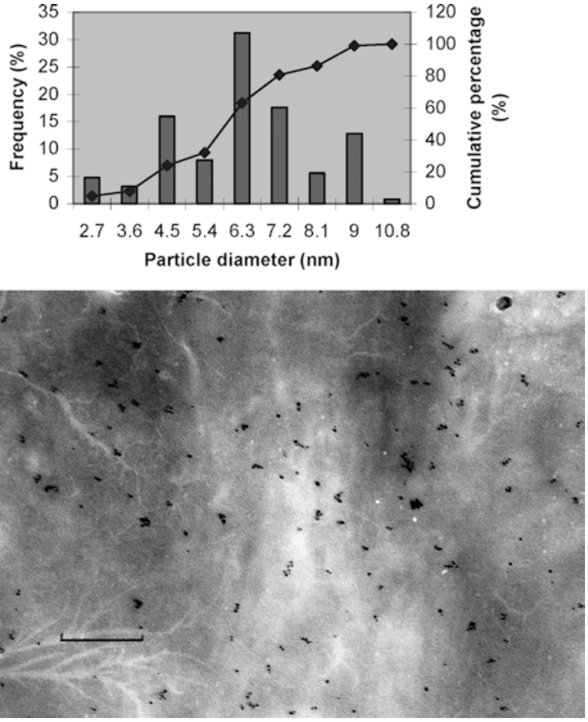

Fig. 2 Particle size distribution and TEM image for sample 1, catalyst immobilized by PVPr with polymer/metal (P/M) mass ratio of 40:1. The length of the *bar* in this figure and the following figures corresponds to 182 nm

Figures 4 and 5 show the TEM morphological results for samples 3 and 4, which were palladium colloids immobilized by two samples of PEOX having $M_w \sim$ 50 000 and 200 000 g/mol, respectively. The most commonly occurring particle sizes were 1.8 and 2.7 nm from the higher-M_w polymer, and these values are smaller than those for sample 3 (2.7 and 4.5 nm), but there was evidence for many aggregates and agglomerates. Longer polymer chain backbones may have coiled around the nanoparticles, which could have led to larger clusters. This observation is in agreement with previously published results in that the use of very high molecular weight polymers to immobilize metal particles tends to favor the formation of agglomerates [2].

Selectivity in hydrogenation processes

The bond dissociation enthalpy at room temperature of H_2 is rather high, at 436 kJ/mol [38]. Consequently, activation of the hydrogen molecule is necessary for reactivity. The activation energy for the substrate (unsaturated reactant) is controlled by the catalyst type,

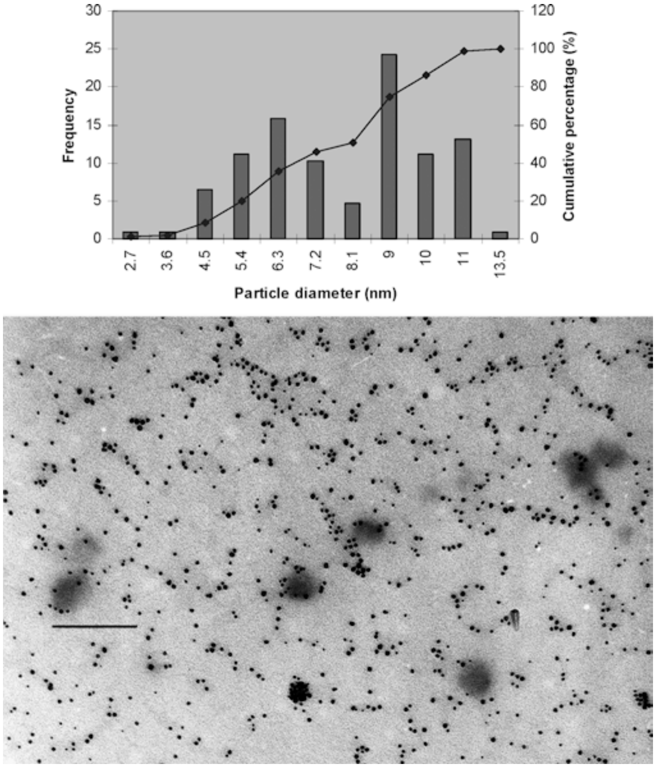

Fig. 3 Same information as in Fig. 2, but showing the effects of increasing the P/M ratio to 80:1 (sample 2)

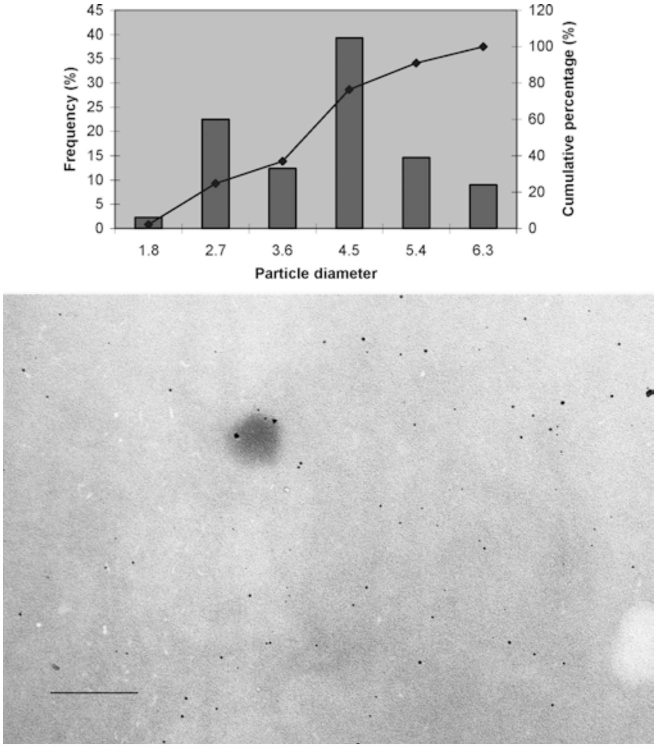

Fig. 4 Particle size distribution and TEM image for sample 5, catalyst immobilized by PEOX with $M_w = 50\ 000$ g/mol and with P/M ratio of 40:1

substrate nature, and reaction conditions. If the substrate adsorption tendency is high, molecules of H_2, substrate, and solvent arrange simultaneously on the catalyst surface, which increases the activation energy. A further increase in the adsorption capacity of the substrate results in a limited H_2 adsorption. For example, the adsorptive displacement of hydrogen from the catalyst surface by diene has been observed for Ni catalysts [39]. A change in the hydrogen-surface bond energy may thus lead to a significant change in hydrogenation selectivity. Relevant specific energy values such as H_2 sorption heats, H_2-surface bond energies, and electronic work functions have been reported elsewhere for Pt-group metals [40]. In the case of two or more reactants, a selective reaction will be observed if there is a significant difference in adsorption ability between the reactants. Selectivity due to adsorptive displacement of olefins by dienes was observed in the Pd-catalyzed hydrogenation reactions of binary mixtures of olefins with dienes [35]. The selectivity was found to be dependent on the difference in surface affinity of alkyne and alkenes in the case of partial hydrogenation of alkyls [41]. There may be four requirements for a heterogeneous catalyst to provide optimal selectivity [42]: a balance between bond strength, the ability to supply specific substrate coordination, the possibility of active ensemble formation, and possibly a template effect. All these parameters depend on both the electronic and geometric properties of the metal particles. The focus here was the ability of the immobilized catalysts to selectively hydrogenate a particular olefin in a reaction containing more than one reactant. Selectivity was evaluated by comparisons of the hydrogenation conversions.

Effects of polymer concentration on geometric selectivity

Of interest here is selectivity with regard to geometric isomers. In general, the rate of alkene hydrogenation has been reported to decrease with increase in length of the olefin chain for both linear molecules and cycloolefins. [41, 43]. However, the data reported for hydrogenations of geometric isomers are rather discrepant. For instance, the rate of 1-hexene hydrogenation was eighteen times greater than that of 2-hexene or cyclohexene by Pt bound to polystyrene modified with dipyridine. However, the same reaction catalyzed with a similar Pd catalyst had a hydrogenation rate for 1-hexene that was only two times greater than that of 2-hexene, and 1.7 times greater than that of cyclohexene [1].

Similar effects were observed in this study, as illustrated in Table 2. In reactions containing two olefins, the rates for cyclic olefins were smaller than those for their non-cyclic counterparts, and increase in the size of the

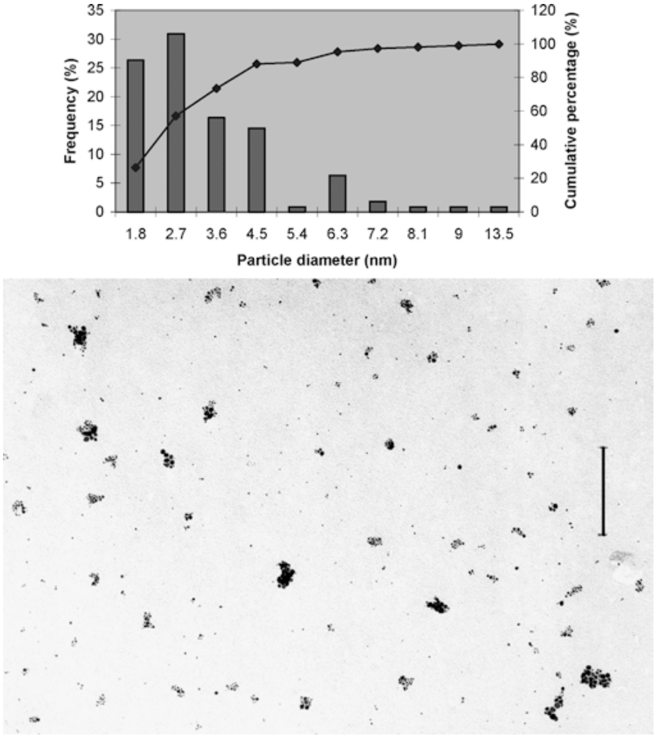

Fig. 5 Same information as in Fig. 4, but showing the effects of increasing M_w to 200 000 g/mol (sample 7)

Table 2 Hydrogenation conversions[a]. Effects of polymer loading

Immobilizing polymer, polymer/metal ratio	1-Octene	Cyclooctene
PVPr, 40/1	100	75.5
PVPr, 80/1	100	20.0
	Cyclohexene	Cyclooctene
PVPr, 40/1	40.0	29.0
PVPr, 80/1[b]	8.6	9.5

[a] Values of % hydrogenated olefins; 0.2 mL olefin, 0.24 mg Pd, 30 psi hydrogen pressure, and 1 h reaction time

[b] 30 min reaction

cyclic olefins led to a decreased hydrogenation rate. For example, palladium colloids immobilized by PVPr with P/M ratio 40:1, gave conversions in the hydrogenation of geometrical isomers *n*-octene and cyclooctene of 100 and 75.5%, respectively. Smaller cyclic olefins had slightly greater hydrogenation rates when reduced using the same catalyst. For example, the conversion for cyclohexene was 40%, but only 29% for cyclooctene. The hydrogenation rate for cyclooctene was smaller in the reaction containing cyclohexene than that in the reaction containing 1-octene. The presence of cyclohexene may affect the hydrogenation rate of cyclooctene, by reducing cyclooctene-metal coordination. This effect was also observed for catalysts immobilized by PEOX, as discussed below.

Table 3 Effects of substrate size

Catalyst/immobilizing polymer	Cyclohexene	Cyclooctene
1/Poly(*n*-vinylpyrrolidone)	40.0	29.0
3/Poly(2-ethyl-2-oxazoline)	59.5	45.7
	1-Hexene	1-Octene
1/Poly(*n*-vinylpyrrolidone)	100	100
3/Poly(2-ethyl-2-oxazoline)	100	100

When the P/M ratio was increased to 80:1, the hydrogenation rates for cyclic olefins decreased. It is possible that this was due to steric hindrance on the cyclic olefin through changes in diffusion rates. The hydrogenation rate, in general, decreases with increasing catalyst particle size, as illustrated here by differences from the particle size of sample 2 being larger than that of sample 1. Earlier studies indicated that non-cyclic olefins were less sensitive to changes of particle sizes than cyclic olefins [40, 43, 44]. The results clearly demonstrated that the hydrogenation rates of some olefins and the selectivity of some hydrogenation reactions can be controlled by changing the amounts of polymer coating.

The conversions of smaller cyclic olefins were greater for catalysts immobilized by either PVPr or PEOX, as shown in Table 3. However, this effect was not observed for non-cyclic counterparts. In general, the hydrogenation rates for 1-hexene and 1-octene were much higher than for the cyclic counterparts. For example, the relative hydrogenation rates were reported to be 1.00 for 1-hexene, 0.99 for 1-octene and 0.63 for cyclohexene in a substrate reaction catalyzed by palladium-containing polyurethane catalyst [45, 46].

The conversions of 1-octene or *trans* 3-octene were both 100% for Pd catalyst treated with PVPr or PEOX. Meanwhile, for single-reactant hydrogenations, the rate of 1-hexene was reported to be higher than that of 2-hexene [4, 47, 48]. Homogeneous olefin hydrogenations by ruthenium complexes [49] or rhodium complexes [50] showed that the hydrogenation rate of terminal alkenes was greater than that of internal alkenes. A significantly shortened reaction time or an extensive kinetic study would be required to reliably document possible differences of this type.

Effects of polymer molecular weight on geometrical selectivity

Results in Table 4 show a decrease in conversion with increasing molecular weight of polymer. The fact that there is any change at all indicates the particles are indeed covered by a layer of polymer with the potential to use it to change efficiency and selectivity. A similar observation was reported for a single-reactant reaction catalyzed by a similar catalyst. Specifically, the conver-

Table 4 Effects of polymer molecular weight

Sample/PEOX M_w (g/mol)	Cyclohexene	Cyclooctene
3/M_w = 50 000	59.5	45.7
4/M_w = 200 000	12.3	9.0
	1-Hexene	Cyclohexene
3/M_w = 55 000	100	100
4/M_w = 200 000	100	17.6

Table 5 Effects of polymer structure

Sample/polymer	1-Octene	Cyclooctene
1/Poly (*n*-vinylpyrrolidone)	100	75.5
3/Poly(2-ethyl-2-oxazoline)	100	53.4
	Cyclohexene	Cyclooctene
1/Poly(*n*-vinylpyrrolidone)	40.0	29.0
3/Poly(2-ethyl-2-oxazoline)	59.5	45.7
	1-Hexene	Cyclohexene
1/Poly (*n*-vinylpyrrolidone)	100	100
3/Poly(2-ethyl-2-oxazoline)	100	100

sion of cyclohexene was reported to decrease when the molecular weight of the polymer was increased from 40 000 to 500 000 g/mol [13]. The molecular weight of the polymer had different effects on selectivity depending on the nature of the other reactant in a two-reactant hydrogenation. The increase in the M_w of PEOX from 55 000 to 200 000 g/mol did not affect selectivity in the hydrogenation of cyclohexene and cyclooctene. It did, however, improve the selectivity in the hydrogenation of 1-hexene and cyclohexene, as indicated by a decrease in conversion from 100 to 17.6%.

Effects of polymer structure

Better selectivity was obtained for catalysts immobilized by PEOX in the reaction mixture *n*-octene and cyclooctene, as indicated in Table 5. However, it is difficult to draw conclusions on the corresponding differences from the data shown for mixtures of cyclohexene vs. cyclooctene, or 1-hexene vs. cyclohexene. The nature of the immobilizing polymer and the presence of the other reactant certainly affect the hydrogenation rate by changing substrate coordinations (resulting from changes in particle surface characteristics), or activation energies, or diffusion rates, as already mentioned.

Conclusions

Colloidal palladium nanocatalysts prepared by in situ reductions of palladium chloride were immobilized and protected by two water-soluble polymers. These polymer-treated catalysts showed high selectivities in hydrogenations of cyclic and noncyclic olefin molecules. However, relatively low selectivities were observed in the hydrogenation of iso olefins having different sizes (such as hexene and octene), or with different positions of the double bond (such as 1-octene and 3-octene). Selectivity was promoted and enhanced by increasing the amounts of the modifying polymers. Further studies would be needed to clarify the separate effects of immobilization and morphology of the catalysts on their efficiencies and selectivities in general.

Acknowledgements We would like to thank Professor Randal Morris in the Department of Cell Biology, College of Medicine, for his support in obtaining transmission electron microscopy images. It is also a pleasure to acknowledge the financial support provided by the National Science Foundation through Grant DMR-0075198 (Polymers Program, Division of Materials Research).

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