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## Activity and selectivity of colloidal platinum nanocatalysts for aqueous phase cyclohexenone hydrogenation

Nathan E. Musselwhite, Sarah B. Wagner, Kimberly A. Manbeck, Lindsay M. Carl, Kyle M. Gross, Anderson L. Marsh\*

Department of Chemistry, Lebanon Valley College, 101 N. College Ave., Annville, PA 17003, USA

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### ABSTRACT

The effect of varying the particle size of poly(vinylpyrrolidone)-capped colloidal platinum nanocatalysts, synthesized in the 1–10 nm size range, on the activity and selectivity during the aqueous-phase hydrogenation of cyclohexenone was investigated. For all particle sizes utilized, products observed during the reaction in order of increasing selectivity were cyclohexenol, cyclohexanol, and cyclohexanone. Selectivity for the unsaturated alcohol (cyclohexenol) was found to be highest for the smallest-sized nanocatalyst, whereas selectivity for the saturated ketone (cyclohexanone) was found to be highest for the largest-sized nanocatalyst. Activities for cyclohexenone hydrogenation were observed to increase with increasing particle size, yet apparent activation energies were determined to be similar for 2.9–7.1 nm nanocatalysts, likely indicating that the same surface reaction is kinetically favored on these nanocatalyst surfaces. Attenuated total reflectance infrared (ATR-IR) spectroscopic measurements on adsorbed cyclohexenone suggest the  $\eta_1(C=0)$  form is more prevalent on the smaller sized nanocatalysts, while the  $\eta_2(C=C)$  and  $\eta_4(C=0, C=C)$  forms are more preferred on the larger sized nanocatalyst. The findings presented herein provide further evidence that structure sensitivity in ketone hydrogenation reactions is linked with catalyst surface structure and adsorbate orientation.

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### 1. Introduction

Selective hydrogenations using platinum catalysts play a valuable role in many chemical industries, ranging from petrochemicals to pharmaceuticals [1,2]. Chemoselective hydrogenations involving unsaturated ketones and aldehydes are of particular interest [3]. For example, the C=C bond in oxosteriods may be hydrogenated over TiO<sub>2</sub> supported Pt catalysts [4]. Many of these reactions are operated in the liquid phase using organic solvents and at much lower temperatures than those for gas-phase reactions, thus increasing selectivity due to a decrease in the occurrence of side reactions [5]. To operate under more environmentally friendly conditions it would be desirable to utilize aqueous media instead of organic solvents [6]. Improvement of catalyst performance under these reaction conditions requires tailoring of material properties through synthetic methods, such as those from colloidal nanoscience [7,8]. The nanocatalysts prepared using these methods are composed of transition metal nanoparticles with a narrow size distribution and typically are capped with organic polymers or dendrimers to prevent aggregation in solution. The solubility of the nanocatalyst may be tailored for water by selecting a capping agent such as poly(vinylpyrrolidone), or PVP. Reports of hydrogenations involving these nanocatalysts dispersed in water have been limited, however [9,10].

In a prior study by our group, platinum nanocatalysts prepared with colloidal nanoscience methods were used to examine the effect of changing nanocatalyst properties (particle size and capping agent molecular weight) and reaction conditions (temperature, hydrogen pressure, and reactant concentration) during the hydrogenation of cyclohexanone [10]. In all reactions carried out, 100% selectivity for cyclohexanol formation was observed, with no side products from decomposition reactions detected. Measured turnover frequencies were seen to increase with increasing particle size, but were found to show no trend with regards to capping agent molecular weight. From the results of temperature studies, similar apparent activation energies in the 21-24 kJ/mol range were determined for the particle sizes employed. A rate law was derived from pressure and concentration studies in which the reaction order with respect to hydrogen is 0.3 and the reaction order with respect to cyclohexanone is 0.8. This rate law is consistent with a Langmuir-Hinshelwood mechanism in which both molecules have low adsorption and one of the molecules (hydrogen) exhibits dissociative adsorption. Attenuated total reflectance infrared (ATR-IR) spectroscopic measurements support the determined rate law, with two peaks observed in the spectrum in the C=O stretching region, suggesting that cyclohexanone in solution exists in equilib-

<sup>\*</sup> Corresponding author. Tel.: +1 717 867 6149; fax: +1 717 867 6075. *E-mail address*: marsh@lvc.edu (A.L. Marsh).

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rium with cyclohexanone adsorbed on the Pt nanocatalyst surface. It is evident that results from experimental work done using these prepared nanocatalysts increase the molecular-level knowledge of catalyst properties that influence reaction selectivity.

In the work presented here, we extend our investigations of aqueous phase hydrogenations using PVP-capped platinum nanocatalysts to the hydrogenation of the unsaturated ketone cyclohexenone, which has been identified as a product of the gasification of biomass [11]. Prior studies of the hydrogenation of cyclohexenone have been limited [12–19], particularly those under more environmentally friendly reaction conditions [16-19]. After synthesis and characterization, Pt nanocatalysts in the 1-10nm size range were employed in aqueous phase hydrogenations. Reaction compositions were found from gas chromatography/mass spectrometry (GC/MS) measurements, which allowed turnover frequencies (TOFs) and reaction selectivities to be determined as a function of particle size. In addition, apparent activation energies were calculated from the temperature dependence of TOFs. ATR-IR spectroscopy was used to elucidate preferred adsorption modes of cyclohexenone on the nanocatalyst surfaces. The experimental findings were then utilized in developing a molecular level model of the effects of changing particle size on selectivity towards specific reaction pathways during hydrogenation.

### 2. Experimental

Poly(vinylpyrrolidone) of 29,000 g/mol molecular weight, hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6 H<sub>2</sub>O), ethylene glycol, and 2-cyclohexen-1-one ( $\geq$ 95%), were obtained from Aldrich. ACS grade methanol and acetone were acquired from PHARMCO, while research purity hydrogen was purchased from Airgas. All chemicals were used without purification. A Millipore Direct-Q system was used to generate 18 M $\Omega$  deionized water for nanocatalyst synthesis and reaction studies.

Specific details for the synthesis of each size of nanocatalyst are described in our prior publication [10] and are based on published literature methods [20,21]. Nanocatalysts were characterized at The Penn State College of Medicine's Electron Microscopy Laboratory using a JEOL JEM-1400 transmission electron microscope. For TEM measurements, colloidal platinum nanocatalyst solutions were placed dropwise onto carbon-coated copper grids. A minimum of 200 particles were counted during size determinations.

Cyclohexenone hydrogenation reactions were performed in a Parr 4566 mini benchtop reactor with constant stirring at 1000 rpm, as previously described for cyclohexanone hydrogenation [10]. To charge the reactor, a selected volume of the Pt colloid solution was mixed with a solution of cyclohexenone in deionized water to give a 1000:1 mole ratio of cyclohexenone to platinum. The reactor was heated to the selected temperature, flushed with hydrogen, and then pressurized to 2.1 bar. At selected reaction times small aliquots (<1 mL) of the reaction mixture were sampled and the platinum nanocatalysts were removed by subsequent centrifugation. Using integrated peak areas obtained from GC/MS (Agilent 6890/5973, Supelcowax 10 column,  $15.0 \text{ m} \times 100 \text{ }\mu\text{m} \times 0.10 \text{ }\mu\text{m}$ ) analysis of reaction samples, the composition in mole percent of the reaction mixture was calculated for each kinetic run. The reaction selectivity of each product,  $S_i$ , was found by taking a ratio of the mole percent of that product,  $x_i$ , to the total mole percent of products, as shown by Eq. (1):

$$S_i = \frac{x_i}{\sum_i x_j} \tag{1}$$

TOFs were calculated by dividing the moles of cyclohexenone reacted by the moles of platinum, and then normalized through division by dispersion factors calculated using TEM particle sizes, as done for our cyclohexanone hydrogenation studies [10].

Cyclohexenone adsorption employing ATR-IR spectroscopy was performed using a Nicolet 380 Fourier-Transform infrared spectrometer fitted with a Specac Gateway ATR optics assembly and flow cell containing a ZnSe crystal, where 64 scans were acquired at 4 cm<sup>-1</sup> resolution with an ATR correction. Nanocatalyst solutions were pumped through the cell from a reservoir using a peristaltic pump as a small volume (<1 mL) cyclohexenone was added to the solution in the reservoir. To remove contributions from water and PVP, difference spectra were carefully calculated by subtracting the spectra for the corresponding platinum colloid solutions from the spectra for the platinum colloid solutions after cyclohexenone addition.

### 3. Results and discussion

Displayed in Fig. 1 are the TEM image and the corresponding histogram for platinum nanocatalysts synthesized with methanol as a reducing agent. The average size of these nanocatalyst particles (together with one standard deviation) was determined to be  $2.9 \pm 0.1$  nm. TEM images and corresponding histograms for platinum nanocatalysts synthesized via other routes may be found in Figs. S-1–S-3 of the supplementary data. Average sizes of these nanocatalyst particles (together with one standard deviation) were calculated to be  $1.7 \pm 0.2$  nm,  $3.6 \pm 0.2$  nm, and  $7.1 \pm 0.3$  nm, respectively. All of the TEM particle sizes reported in this work agree well with those reported in the literature for platinum nanoparticles prepared using these colloidal-based synthetic methods [10,21]. Hereafter these colloidal platinum nanocatalysts are referred to by these TEM sizes.

After characterization, the synthesized nanocatalyts were dispersed in water and subsequently utilized in the hydrogenation of cyclohexenone (CHEO), the reaction pathways of which are shown in Scheme 1. In the upper pathway cyclohexanone (CHO) is formed, whereas in the lower pathway cyclohexenol (CHEOL) is produced. Both of these products may undergo further hydrogenation to cyclohexanol (CHOL). Displayed in Fig. 2 is a plot of compositions in mole percents as a function of reaction time for a hydrogenation reaction using 7.1 nm colloidal Pt nanocatalysts that was carried out at a temperature of 323 K, a hydrogen pressure of 2.1 bar, and a cyclohexenone to platinum mole ratio of 1000:1. As seen in the figure, the fraction of cyclohexenone decreases steadily over the course of the reaction, while the fraction of cyclohexanone increases gradually. During the initial stage of the reaction small fractions of cyclohexenol and cyclohexanol are formed. At longer reaction times, the fraction of cyclohexenol decreases to zero and the fraction of cyclohexanol increases, likely due to the hydrogenation of both cyclohexenol and cyclohexanone. Still, based on the data, as presented in the figure, the dominant reaction channel appears to be the hydrogenation of cyclohexenone to cyclohexanone.

To better understand the effect of particle size on the distribution of products during the course of the reaction, experiments were performed using nanocatalysts with selected particle sizes synthesized over the 1–10 nm size range. Turnover frequencies based on the amount of cyclohexenone reacted and product selectivities were calculated using mole percents determined at around 40% conversion. Summarized in Table 1 are percent selectivities for the products cyclohexanone, cyclohexenol, and cyclohexanol calculated for hydrogenation reactions performed at 308 K and 2.1 bar hydrogen with colloidal platinum nanocatalysts of selected sizes. In general, the percent selectivity for cyclohexanone increases from

# a 25 nm



**Fig. 1.** Representative (a) TEM image and (b) corresponding histogram for 2.9 nm colloidal platinum nanocatalysts capped with 29,000 g/mol PVP.



Scheme 1. Reaction pathways in the hydrogenation of cyclohexenone.

#### Table 1

Percent selectivities, turnover frequencies, and activation energies for selected sizes of 29,000 g/mol PVP-capped Pt nanocatalysts. Reaction conditions were 2.1 bar  $H_2$  and a 1000:1 mole ratio for cyclohexenone to Pt. The percent selectivities and turnover frequencies are values at 40% conversion for reactions carried out at 308 K.

d <sub>TEM</sub> (nm)	Dispersion factor (D)	% S <sub>CHO</sub>	% S <sub>CHEOL</sub>	% S <sub>CHOL</sub>	$\begin{array}{c} \text{TOF} \\ (\text{mol}_{\text{CHEO}} \\ \\ \\ \text{reacted} \ \text{mol}_{\text{surface}} \\ \\ \text{Pt}^{-1} \ \text{s}^{-1} ) \end{array}$	E <sub>a</sub> (kJ/mol)
1.7	0.80	86	4	10	0.26	42
2.9	0.47	89	0	11	0.33	21
3.6	0.38	88	1	11	0.40	20
7.1	0.19	91	2	7	0.67	21

86% to 91% with an increase in particle size from 1.7 nm to 7.1 nm, whereas the percent selectivity for cyclohexenol decreases from 4% to 2% with an increase in particle size from 1.7 nm to 7.1 nm. The percent selectivity for cyclohexanol also decreases, going from around 10% to around 7% with an increase in particle size from 1.7 nm to 7.1 nm. The observed percent selectivities for cyclohexanone are similar to those reported previously in the literature for hydrogenations using platinum catalysts [12,14,17,18]. In each instance the authors report cyclohexanol as the only other major product; no unsaturated alcohol was found. Conversely, increased selectivity to the unsaturated alcohol was seen during the gas phase hydrogenation of crotonaldehyde for larger particle sizes [22,23]. Here the authors attribute this trend to an increased number of active sites on the Pt particle surfaces since larger particles would be more capable of interacting with both the C=O and C=C groups.

For cyclohexenone hydrogenation, a similar trend was also observed with regards to measured TOF values. In comparing the TOFs described in this work across nanocatalyst particle sizes, as shown in Table 1, it is apparent that the TOF for the hydrogenation of cyclohexenone increases with an increase in particle size at this reaction temperature. This same increase in TOF with an increase in



**Fig. 2.** Compositions in mole percents during hydrogenation of cyclohexenone using 7.1 nm colloidal platinum nanocatalysts. Reaction conditions were 323 K, 2.1 bar hydrogen, and a cyclohexenone to platinum mole ratio of 1000:1.



**Fig. 3.** Arrhenius plots for cyclohexenone hydrogenation over the 308–338 K temperature range using nanocatalysts with selected Pt particle sizes. Reaction conditions were 2.1 bar hydrogen and a cyclohexenone to platinum mole ratio of 1000:1.

particle size was observed for the hydrogenation of cyclohexenone over Pt nanoparticles supported on bentonite [14], as well as for the hydrogenation of cyclohexanone using these colloidal PVP-Pt nanocatalysts [10] and for the hydrogenation of crotonaldehyde over supported Pt catalysts [22,23]. In the case of crotonaldehyde hydrogenation, the authors postulate that an increase in particle size leads to an increase in the number of active sites for hydrogenation, mainly (111) oriented terrace sites. Nanocatalysts synthesized with largely (111) terraces exposed were reported to be more active for aldehyde hydrogenation than those with largely (100) terraces exposed [24]. In the case of PVP-capped Pt nanocatalysts suspended in water, it is expected that (111) terrace sites are open on the platinum surface for all particle sizes prepared [8]. The PVP groups might be interacting with the defect sites on the surface, leaving the terrace sites open, as indicated by previous ATR-IR measurements of adsorbed CO [10]. The smaller sized nanocatalysts would be expected to contain a higher concentration of defect sites, which would not be active for hydrogenation, than a higher concentration of terrace sites. Although the change in TOF with a change in Pt nanocatalyst particle size perhaps suggests the reaction is structure sensitive, dispersion factors for the smaller sized nanocatalysts may be overestimated due to the lower concentration of terrace sites.

Additional experiments were also conducted over the temperature range 308–338 K for each nanocatalyst particle size in order to determine apparent activation energies. Hydrogenations were carried out at selected temperatures with a hydrogen pressure of 2.1 bar and a cyclohexenone to platinum mole ratio of 1000:1. In general, the results of these experiments indicate that the TOF increased as the reaction temperature was increased for all of the particle sizes studied. Apparent activation energies for hydrogenations carried out with nanocatalysts of selected particle sizes were determined using the Arrhenius plots shown in Fig. 3. As seen in the figure, the reactions exhibited Arrhenius behavior over the temperature range employed in the studies. Linear regression analysis of the data in the Arrhenius plots resulted in similar apparent activation energies over the 2.9 to 7.1 nm particle size range, as seen in Table 1. The calculated apparent activation energies of around 20 kJ/mol for particle sizes of 2.9, 3.6, and 7.1 nm are close to the value of 20.9 kJ/mol reported for the hydrogenation of cyclohexenone on a supported Rh catalyst [13] and are slightly lower than the value of 25 kJ/mol measured for the liquidphase hydrogenation of cyclohexene over a Pt foil catalyst [25]. The value of 42 kJ/mol determined for hydrogenations using the 1.7 nm nanocatalysts indicates that the reaction on these particles is more sensitive to changes in temperature. It is probable that this change in apparent activation energy results from a change in adsorption energy on the smaller sized nanocatalysts. In an effort to understand the details of the reactions described by these apparent activation energies, a kinetic analysis of the reaction data was carried out.

In order to perform the kinetic analysis, the reaction data presented in Fig. 1 were modeled using Euler's method of approximation [26]. The following reactions were considered in the model:

Cyclohexenone 
$$\stackrel{k_1}{\longrightarrow}$$
 Cyclohexanone  
Cyclohexenone  $\stackrel{k_2}{\longrightarrow}$  Cyclohexenol  
Cyclohexanone  $\stackrel{k_3}{\longrightarrow}$  Cyclohexanol  
Cyclohexenol  $\stackrel{k_4}{\longrightarrow}$  Cyclohexanol

These reactions were then used to create the following set of differential equations to describe the reaction rates:

$$\frac{dC_1}{dt} = -k_1C_1 - k_2C_1 
\frac{dC_2}{dt} = k_1C_1 - k_3C_2 
\frac{dC_3}{dt} = k_2C_1 - k_4C_3 
\frac{dC_4}{dt} = k_3C_2 + k_4C_3$$
(3)

In these equations,  $C_1$ ,  $C_2$ ,  $C_3$ , and  $C_4$  are the concentrations of cyclohexenone, cyclohexanone, cyclohexenol, and cyclohexanol, respectively. The initial conditions were set such that, at time = 0,  $C_1 \neq 0$  and  $C_2 = C_3 = C_4 = 0$ . The model provides reasonable fits to the experimental data, as seen by the dashed lines shown in Fig. 2. The values for the rate constants were then multiplied by the mole ratio factor of 1000 and normalized by dispersion factors to estimate TOFs for the various reaction channels. For the first pathway, the hydrogenation of cyclohexenone to cyclohexanone, a TOF of 1.4 mol<sub>CHO</sub> mol<sub>surface Pt</sub><sup>-1</sup> s<sup>-1</sup> was estimated. For the second pathway, the hydrogenation of cyclohexenone to cyclohexenol, a TOF of  $0.068 \text{ mol}_{CHEOL} \text{ mol}_{surface Pt}^{-1} \text{ s}^{-1}$  was predicted. This TOF for C=O hydrogenation is lower than that determined in the case of cyclohexanone hydrogenation [10], which likely indicates that the presence of the C=C bond slows down the rate of C=O hydrogenation. The sum of the two calculated values is higher than the experimental value of 0.79 mol<sub>CHEO reacted</sub> mol<sub>surface Pt</sub><sup>-1</sup> s<sup>-1</sup> for the total hydrogenation calculated at 40% conversion of cyclohexenone. It is interesting to note the TOF for the first channel is around 20 times higher than that for the second channel, consistent with a reported observation for the hydrogenation of crotonaldehyde on a Sn/Pt(111) single crystal catalyst [27]. In the case of further hydrogenation, a TOF of 0.13 mol<sub>CHO</sub> reacted mol<sub>surface Pt</sub><sup>-1</sup> s<sup>-1</sup> for cyclohexanone to cyclohexanol was calculated, whereas a TOF of 13 mol<sub>CHEOL reacted</sub> mol<sub>surface Pt</sub><sup>-1</sup> s<sup>-1</sup> for cyclohexenol to cyclohexanol was determined. The value for cyclohexanone hydrogenation is close to that observed in our previous study mentioned earlier [10]. These findings clearly suggest that relative surface reaction



**Fig. 4.** ATR-IR spectrum of the carbonyl stretching region for cyclohexenone in the presence of 2.9 nm Pt nanocatalysts capped with 29,000 g/mol PVP.

rates play a key role in determining reaction selectivity during the hydrogenation of cyclohexenone.

In addition to a range of kinetic studies, spectroscopic experiments were also carried out to verify preferred adsorption modes for cyclohexenone on the Pt nanocatalyst surfaces. Displayed in Fig. 4 is the carbonyl region of an ATR-IR spectrum of cyclohexenone in the presence of 2.9 nm Pt nanocatalysts dispersed in water. Peak assignments were made based on comparisons with literature data [28,29] and vibrational modes calculated at the B3LYP level of theory with the 6-31G basis set and water as the solvent using Gaussian 03 [30]. These peak assignments are summarized in Table 2. As seen in the figure, there is a broad strong peak at 1651 cm<sup>-1</sup>, which is assigned to the C=O stretching and C=C stretching modes. It is likely that this band is the result of the overlap of the two, and that the C=O stretching mode is the dominant contribution. The C=O stretching vibrational frequency is also likely red-shifted from the value for the gas phase molecule, suggesting that the molecule is interacting with the Pt nanocatalyst surface through the carbonyl group. The bands at 1458 and 1425 cm<sup>-1</sup> are assigned to  $CH_2$  scissoring modes, while the band at 1396 cm<sup>-1</sup> is assigned to

### Table 2

Experimentally observed vibrational frequencies in the  $1750-1250 \text{ cm}^{-1}$  region of the ATR-IR spectrum for cyclohexenone in the presence of 2.9 nm colloidal platinum nanocatalysts capped with 29,000 g/mol PVP and dispersed in water. Also included are vibrational frequencies, calculated at the B3LYP level of theory with the 6-31G basis set and water as the solvent, and normal mode assignments.

$\tilde{\nu}_{exp}(cm^{-1})$	$\tilde{\nu}_{calc} \left( cm^{-1} \right)$	Normal mode assignment
1651	1736	C=O stretching
	1679	C=C stretching
	1517	CH <sub>2</sub> scissoring
1458	1485	CH <sub>2</sub> scissoring
1425	1476	CH <sub>2</sub> scissoring
1396	1424	CH wagging



Scheme 2. Possible adsorption modes for cyclohexenone on a Pt surface.

CH wagging modes. Similar results were also found for the 1.7 nm and 3.6 nm Pt nanocatalysts; however, a much weaker band for the C=O stretching mode was observed for the 7.1 nm Pt nanocatalysts. These spectroscopic results will be combined with the kinetic results to develop a molecular-level picture of the factors influencing activity and selectivity for this catalytic reaction.

Reported findings from theoretical calculations suggest that adsorption modes of the aldehvdes play a role in influencing reaction selectivity towards the unsaturated alcohol versus the saturated aldehvde [31,32]. For cyclohexenone three possible adsorption configurations may be considered, as depicted in Scheme 2. The first adsorption mode, an  $\eta_1$ (C=O) configuration shown in Scheme 2a, consists of the carbonyl group interacting with the Pt nanocatalyst surface with the ring normal to the surface. The second binding configuration, an  $\eta_2$ (C=C) configuration shown in Scheme 2b, consists of the vinyl group interacting with the Pt nanocatalyst surface with the ring normal to the surface. The third adsorption mode, an  $\eta_4$  (C=O, C=C) configuration shown in Scheme 2c, consists of the carbonyl and vinyl groups interacting with the Pt nanocatalyst surface with the ring parallel to the surface. Using surface vibrational selection rules [33], the C=O stretch should only be visible in the ATR-IR spectrum in the configuration shown Scheme 2a. Based on the ATR-IR data presented here, this adsorption mode is likely present in higher concentrations on the smaller sized nanocatalyst surfaces, whereas the other two modes may be found in higher concentrations on the 7.1 nm nanocatalyst surface. The configuration in Scheme 2b would almost certainly lead to hydrogenation of the vinyl group, and since results from the kinetic modeling show that the rate of C=C hydrogenation is much faster than the rate of C=O hydrogenation, it is likely that only the vinvl group would be hydrogenated in Scheme 2c. Any unsaturated alcohol that forms, then, would be the result of the reaction of cyclohexenone while adsorbed in the configuration shown in Scheme 2a, particularly since the kinetic modeling results indicate this reaction step to be the slowest out of the four. The kinetic modeling results also seem to suggest that any unsaturated alcohol that forms would be immediately hydrogenated to the saturated alcohol. Findings from previous studies showed that the addition of a small amount of NaOH to the reaction mixture inhibits this pathway during cinnamaldehyde hydrogenation, thereby increasing unsaturated alcohol selectivity [34,35]. The lower selectivity of cyclohexenol in the present work, then, may likely be the result of further hydrogenation to form the saturated alcohol.

### 4. Conclusions

PVP-capped colloidal platinum nanocatalysts were synthesized in the 1–10 nm size range and characterized using TEM. The prepared nanocatalysts were active in the aqueous-phase hydrogenation of cyclohexenone and displayed high selectivity for the formation of cyclohexanone. Experiments in which the temperature-dependence of the reaction rate was investigated yielded similar activation energies for particle sizes of 2.9–7.1 nm, indicating that the same reaction channel, cyclohexanone formation, is favored on these nanocatalysts. Results from kinetic modeling of the experimental data provide further evidence for this observation. Still, smaller sized nanocatalysts were more selective for unsaturated and saturated alcohol formation. Findings from ATR-IR experiments clearly suggest that adsorbed configurations of cyclohexenone likely play a role in determining selectivity. Taken together, these results may be used to enhance the knowledge of designing environmentally friendly and efficient routes for manufacturing desired chemical commodities.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.05.033.

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