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Stabilizer substitution and its effect on the hydrogenation catalysis by Au nanoparticles from colloidal synthesis

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Au nanoparticles (NPs) carrying different stabilizers (PVP, PVA and CTAB) were prepared by stabilizer-exchange of

freshly prepared citrate (Citr)-stabilized Au NPs (Au-Citr) with the substitute stabilizers, respectively. The stabilizer

substitutions were monitored with UV-vis spectroscopy and the resultant Au particles were further characterized with FTIR and TEM after they were immobilized on a SiO₂ support. Measurements of the catalytic performance of

the immobilized Au NPs for the hydrogenation reactions of p-chloronitrobenzene and cinnamaldehyde enabled us

to address the impact of stabilizer substitution on the hydrogenation catalysis of Au NPs.

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1. Introduction

Catalysis by supported nanosized Au particles has been an intensive research topic in heterogeneous catalysis during the past two decades because of the richness and unique structure-sensitive properties of Au nanoparticles (NPs) and their related applications in energy conversion, chemical synthesis and abatement of environmental pollutants. Conventional preparations of supported Au catalysts by deposition-precipitation or impregnation make it difficult to avoid size scattering of the Au NPs and to ensure complete reduction of the gold precursor(s). When coupled with more or less metal-support interaction, the widely scattered sizes and reducibility of gold would make it difficult to understand the Au nanosize (and shape) effect and nature of catalytic Au sites.^{1,2} The advantages of using Au NPs from colloidal synthesis are the precisely narrowed size distribution and morphology, usually due to the function of their associated stabilizer (or capping molecules) added in the early stage of the synthesis.³⁻⁵ The stabilizer may serve as a structuredirecting agent by interacting with metal particle and provide electrostatic and/or steric stabilization for the as-prepared NPs.^{3,4} However, a considerable amount of stabilizer can still remain associated with the product Au NPs even after they are immobilized on supporting materials. Interaction between the stabilizer residues and their stabilized Au NPs could lead to steric hindrance to surface Au sites active for catalytic reactions and modification to the surface electronic structure of the Au NPs,⁵⁻⁹ and induce micro-polarity at or around the Au surface,⁷ which could significantly change the catalytic performance of Au NPs, either in their free (in colloidal solution) or immobilized (on a solid support) states.⁵⁻¹⁰

We showed previously that the electrocatalytic properties of nearly monodisperse Au NPs and their derived Pt^Au (Pt-on-Au) nanostructures of similar Pt dispersions were remarkably affected by the nature of the residual stabilizer (PVA, PVP or citrate) involved in the colloidal synthesis of the Au NPs; depending on type of the electrochemical reaction, the stabilizer effect could even significantly outweigh the Au nano-size effect.5 In that work, the stabilizer effects were addressed with similarly sized Au NP samples (with average sizes at around 3.2, 5.0 and 10.0 nm, respectively) synthesized by changing the stabilizer from PVA to PVP or citrate and immobilized on a carbon black support (Vulcan 72).⁵ With the motivation to start from the same Au NPs, we have been attempting to make substitution of the original Au-associated stabilizer moieties from a colloidal synthesis with different substituting stabilizers. We have undertaken to do this by exchanging with a large excess of the substituting stabilizer or by adsorption of the substitute stabilizers upon immobilized clean Au NPs on which the original stabilizer residues had been completely removed by UV-ozone treatment.11 Herein, we report our investigation of the substitution by exchange of Au stabilizer and its effect on the performance of Au NPs for selective hydrogenation reactions. Citrate-stabilized Au NPs (Au-Citr) were used as the starting material as the Citr stabilizer (a tricarboxylate anion) has only weak interaction with Au NPs,^{6,12-15} which can be easily replaced with the substitute stabilizers like cetyltrimethyl ammonium bromide (CTAB), polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVA). Ultraviolet-visible (UV-vis) spectroscopy was used to monitor the stabilizer-substitution process. The resultant stabilizer-carrying Au NPs were immobilized on a noninteracting support (SiO₂) and were characterized by transmission

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electron microscopy (TEM) and infrared (IR) spectroscopy. Hydrogenation reactions of *p*-chloronitrobenzene (*p*-CNB) and cinnamaldehyde (CAL) were conducted to probe the consequences of stabilizer substitution on the catalytic property of Au.

2. Experimental

2.1 Preparation and immobilization of Citr-stabilized Au NPs

The Citr-stabilized Au NPs (Au-Citr, 4.7 \pm 0.9 nm) were prepared by slightly modifying a previously reported procedure.^{5,16} Briefly, a freshly prepared solution of 0.02 M NaBH₄ (2 mL) was injected under stirring into a solution containing 0.25 mM HAuCl₄ (200 mL) and trisodium citrate (Citr/Au = 3 mol/mol) at room temperature. Formation of Au-Citr NPs was observed as soon as the NaBH₄ solution was injected, as characterized by a color change of the solution. Stirring continued for another 5 min after the injection of NaBH₄, and was followed by storing the as-prepared colloidal Au solution at 4 °C for later use.

Immobilization of Au-Citr NPs followed a procedure reported earlier.^{17,18} A desired amount of SiO₂ (Degussa, AEROSIL 90, BET surface area: 90 m² g⁻¹) was added to the as-prepared solution of Au-Citr NPs under vigorous stirring, with the solution pH being adjusted to *ca.* 1.5. The solids were separated by filtration after stirring for 2 h. The filtration produced a colorless filtrate, which indicated a quantitative immobilization of the Au NPs on SiO₂. The Au loading was controlled to be 1 wt%. The solids were extensively washed with deionized water and then dried in air at 110 °C to produce Au-Citr/SiO₂.

2.2 Stabilizer-substitution of Au-Citr NPs

The freshly prepared Au-Citr solution was used to prepare Au NPs carrying different substitute stabilizers [coded as ExStabilizer(Au-Citr)] by an exchange reaction in solution containing a large excess of the substituting stabilizer (PVP, PVA or CTAB), i.e., stabilizer-substitution. Briefly, a desired amount of the incoming stabilizer (PVP, PVA or CTAB) was added into the as-prepared Au-Citr solution and then kept under stirring for 5 h; the overall molar ratio of PVP-monomer/Au, PVA-monomer/Au or CTAB/Au was fixed at 30. UV-vis spectroscopy measurements were carried out at an interval of ca. 1 h to monitor the stabilizer-substitution process. The resultant Au NPs were then immobilized on SiO₂, following the procedure of preparing Au-Citr/SiO2. The product samples were denoted as ExPVP(Au-Citr)/SiO₂, ExPVA(Au-Citr)/SiO₂ or ExCTAB(Au-Citr)/SiO₂, accordingly. A schematic illustration of the sample preparations is given in Fig. 1.

2.3 Characterization methods

UV-vis absorption spectra of the colloidal solutions were measured at room temperature on a Unico UV-2102 PC spectrometer at a resolution of 1 nm. The stabilizer-substitution solutions were sampled at regular intervals in a quartz cell of $4.5 \times 1 \times 1$ cm for measuring the change of the surface plasma resonance (SPR) of Au NPs during the substitution process.

Transmission electron microscopy (TEM) measurements were carried out on a Tecnai G2 F20 U-Twin microscope at



Fig. 1 Schematic illustration of the sample preparations

200 kV. At least 300 particles were randomly measured to determine the mean diameter of Au NPs, using the equation $d = \Sigma(n_i d_i)/\Sigma n_i$, where n_i is the number of particles with a diameter of d_i . The sample powders were dispersed in H₂O, sonicated for *ca.* 0.5 h, then deposited on a copper grid coated with a perforated carbon film, and air-dried at ambient temperature.

Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Perkin Elmer 2000 system. The sample powders were mixed with KBr powders at a mass ratio of 1:12 and then ground and pressed into a wafer for the measurement. The spectra were recorded with a resolution of 4 cm^{-1} from 4000 to 500 cm⁻¹, accumulating 10 scans per spectrum.

2.4 Catalytic hydrogenation reactions of p-CNB and CAL

The hydrogenation reactions were performed in a 25 mL stainless steel autoclave under magnetic stirring (900 rpm), as described previously.18,19 The reactor was loaded with 50.0 mg catalyst and 2.0 mmol p-CNB dissolved in 5 mL toluene (solvent) (molar p-CNB/Au = 800) or 50.0 mg catalyst and 4.0 mmol CAL in 5 mL *p*-xylene (solvent) (molar CAL/Au = 1600). After purging with H₂ (ca. 0.8 MPa) six times, the reactor was pressurized to a desired H₂ pressure (2.0 MPa) and then thermostatted at 150 °C (reaction temperature) to cause the catalytic reaction. Termination of the reaction was carried out by rapidly cooling the reactor with an ice-water bath when the reaction time reached 4 h. After separation from the solid catalyst by filtration, the reacted solution was analyzed on a HP7890 gas chromatograph (GC) equipped with a HiCap CBP20-S25-050 (Shimadzu) capillary column (i.d., 0.32 mm; length, 25 m) and a flame ionization detector (FID). Blank reaction tests with bare SiO₂ but without Au detected no reaction of either p-CNB or CAL. A set of measurements varying the catalyst loading and stirring speed for the reactions showed that our chosen reaction conditions ensured no involvement of mass-transfer limitation during the catalytic reactions, as detailed in our previous work.²⁰

3. Results and discussion

The stabilizer-exchange of Au-Citr NPs with PVP, PVA and CTAB was monitored regularly with UV-vis spectroscopy, as shown in Fig. 2. The dominant absorbance near 518 nm featured the surface plasma resonance (SPR) of Au NPs, arising from the collective oscillation of surface electrons induced by the incident light. This SPR peak would be dependent of the Au size and size-distribution²¹ and could also be affected by the nature of Au-associated stabilizers.^{7,13} The exchange of Au-Citr with either PVP (Fig. 2A) or PVA (Fig. 2B) significantly enhanced the intensity of the SPR peak during the first 5 min, but further extending the exchange time up to 5 h induced little change in this signal. This clearly demonstrates a fast substitution of PVP or PVA for Citr in the initial 5 min. The invariant SPR peak position and shape after an exchange for longer than 1 h would suggest that the substitution of Citr by either PVP or PVA did not result in significant modification of the sizes and size-distribution of Au NPs. In the exchange with CTAB (Fig. 2C), however, the Au SPR peak became not only significantly intensified but also red-shifted to ca. 532 nm in the

initial 5 min following CTAB addition. The intensification of the SPR peak demonstrates a fast substitution of CTAB for the Citr stabilizer of the Au-Citr NPs while the red-shifted peak position hints at a significant aggregation of the Au NPs, which had probably been induced by electrostatic interaction between the positively charged ammonium moieties of CTAB and the more or less negative Au-Citr NPs, with the charge imparted by adsorbed citrate anions as proposed in earlier reports.^{14,22} The SPR peak narrowed and its position more or less blue-shifted on prolonged exchange time up to 5 h; the peak position became stabilized at 528 nm but its components at longer wavelengths (*i.e.*, SPR coupling bands at >600 nm) became less pronounced, which may suggest more or less disassembling of larger Au aggregates that were produced at the initial stage $(\leq ca. 5 \text{ min})$ of the exchange reaction with CTAB. These observations resemble the documentation by Yang et al.23

Shown in Fig. 3 are the sizes and size-distributions of Au in Au-Citr and ExStabilizer(Au-Citr) samples. The measured Au sizes for ExPVP(Au-Citr) were not distinguishable from those for ExPVA(Au-Citr); they were distributed in 4.4 ± 0.9 nm and were comparable to those for the starting Au-Citr NPs (4.7 ± 0.9 nm). While for ExCTAB(Au-Citr), the sizes became significantly larger and scattered (7.1 ± 2.8 nm), demonstrating an apparent aggregation/growth of Au during the exchange with the CTAB stabilizer. These results are consistent with the above analysis of the SPR peaks in the UV-vis spectra.



Fig. 2 UV-vis spectra of Au NPs during the stabilizer-substitution of colloidal Au-Citr with PVP (A), PVA (B) and CTAB (C), as well as the stabilizer-substitution of colloidal Au-PVP with Citr (D).



Fig. 3 Representative TEM images of Au NPs of Au-Citr (A), ExPVP(Au-Citr) (B), ExPVA(Au-Citr) (C) and ExCTAB(Au-Citr) (D).

The Au sizes in the SiO₂-immobilized samples were also measured with TEM, which are shown in Fig. 4. The Au sizes for both the ExPVP(Au-Citr)/SiO₂ (4.7 \pm 0.9 nm) and ExPVA(Au-Citr)/SiO₂ (4.7 \pm 1.1 nm) were found to be comparable with their counterparts before the immobilization (Fig. 3). In contrast, the Au sizes for Au-Citr/SiO₂ (11.6 \pm 6.5 nm) and ExCTAB(Au-Citr)/SiO₂ (8.9 \pm 2.9 nm) became significantly larger and widely scattered when compared to their counterparts before the immobilization. These results indicate that Citr and CTAB were weaker and less efficient stabilizers for Au NPs, compared with PVP and PVA. Therefore, the four stabilizers used in this present study could be ranked in the order of PVP \sim PVA \gg CTAB > Citr, according to their "stabilizing strength". Note that this rank is based on the difference between the Au sizes for the "mobile" Au NPs in the colloidal solution and their immobilized counterparts on the SiO₂ support.

PVA- and PVP-stabilized Au NPs of 4.7 ± 1.0 nm (denoted as Au-PVA and Au-PVP) were synthesized directly by controlled reduction of HAuCl₄ in the presence of PVA^{5,18} and PVP,^{5,21} respectively. Both Au-PVA and Au-PVP NPs were subjected to stabilizer-substitution with citrate, by adding an excess amount of trisodium citrate [Citr/Au (molar) = 30] to the as prepared colloidal solutions of Au-PVA and Au-PVP. Measurements with UV-vis spectroscopy after the addition of citrate detected no significant change in the Au SPR signals of the Au NPs in both cases (Fig. 2D shows as a representative the spectra during the exchange of Au-PVP with Citr), which demonstrates that Citr is a weaker stabilizer than the PVP and PVA polymers. The size and size distribution of Au NPs in the ExCitr(Au-PVA)/SiO2 and ExCitr(Au-PVP)/SiO2 samples were also measured with TEM (Fig. 4E and F), they were very similar to those for their parent Au-PVP and Au-PVA particles (see also Table 1). These data are in line with the relative "stabilizing strength" of PVP, PVA and Citr.



Fig. 4 Representative TEM images of Au NPs of Au-Citr/SiO₂ (A), ExPVP(Au-Citr)/SiO₂ (B), ExPVA(Au-Citr)/SiO₂ (C), ExCTAB(Au-Citr)/SiO₂ (D), ExCitr(Au-PVA)/SiO₂ (E) and ExCitr(Au-PVP)/SiO₂ (F).

 Table 1
 Catalytic data for Au NPs in ExStabilizer(Au-Citr)/SiO₂ samples for p-CNB hydrogenation reaction^a



Catalyst	Au size (nm)	<i>p</i> -CNB conv. (%)	$\begin{array}{l} MSA_{Au} \\ (mol \ h^{-1} \ g_{Au} ^{-1}) \end{array}$	${\mathop{\rm TOF}_{p ext{-CNB}}}{({{ m h}^{-1}})}$	
Au-Citr/SiO ₂	11.6 ± 6.5	3.1	0.03	71	
ExPVP(Au-Citr)/SiO ₂	4.7 ± 0.9	18.5	0.19	182	
ExPVA(Au-Citr)/SiO ₂	$\textbf{4.7} \pm \textbf{1.1}$	22.3	0.22	220	
ExCTAB(Au-Citr)/SiO ₂	8.9 ± 2.9	2.7	0.03	47	
Au-PVA/SiO ₂	4.7 ± 1.0	29.1	0.28	260	
ExCitr(Au-PVA/SiO ₂)	$\textbf{4.8} \pm \textbf{1.4}$	16.7	0.17	161	
Au-PVP/SiO ₂	4.7 ± 1.0	22.3	0.22	218	
ExCitr(Au-PVP)/SiO ₂	5.3 ± 1.2	15.0	0.15	150	

^{*a*} Rxn conditions: 50 mg catalyst, 2 mmol *p*-CNB, 5 mL toluene (solvent), $P_{\rm H_2} = 2$ MPa, 150 °C, 4 h. *p*-CNB/Au (molar) = 800. Only *p*-chloroaniline (*p*-CAN) was detected as the product.

The ExStabilizer(Au-Citr)/SiO $_2$ samples were also characterized with FTIR, the results are shown in Fig. 5. In the



Fig. 5 FTIR spectra of ExStabilizer(Au-Citr)/SiO₂ samples.

spectrum for the ExPVP(Au-Citr)/SiO₂ sample, the absorptions in the region of 3000-2800 cm⁻¹ were characteristic of CH₂ stretching vibrations from the hydrocarbon backbone and the pyrrolidone rings of PVP while the ones in 1500-1400 cm⁻¹ were characteristic of C-N stretching and C-H scissoring vibrations; the strong absorption at 1655 cm⁻¹, was superimposed on the background absorption from the H-O-H bending vibration of adsorbed water molecules on the SiO₂ support (ca. 1630 cm^{-1} , see a spectrum for bare SiO₂ at the bottom), featured the stretching vibration of the C=O groups in the PVP stabilizer. The presence of PVA in the ExPVA(Au-Citr)/SiO2 sample was characterized by CH2 stretching modes at 2925 and 2855 cm⁻¹, CH₂ scissoring at *ca.* 1440 cm⁻¹ (broad) and C-O-H in-plane bending at 1385 cm⁻¹; the stretching vibration of the polar C-O bond (ca. 1050 cm⁻¹) could be overlapped by the strong absorptions of Si-O stretching below 1200 cm⁻¹ from the SiO₂ support. In the spectrum for the ExCTAB(Au-Citr)/SiO₂ sample, the absorptions at 2960, 2925 and 2855 cm⁻¹ (C-H stretching), 1460 and 1385 cm⁻¹ (C-H bending) would denote the alkyl chains in the CTAB stabilizer. The IR spectrum for Au-Citr/SiO2 showed only a weak absorption at 1385 cm⁻¹, arising from the symmetric -COO⁻ vibration; its asymmetric absorption could be immersed in the background absorption from the H–O–H bending vibration (*ca.* 1630 cm⁻¹) of SiO₂ adsorbed water molecules. The bands featuring the C–H stretching vibrations in the region of 3000–2800 cm⁻¹ were essentially invisible, evidencing a very low "density" of Citr in the Au-Citr/SiO₂ sample compared to those of the other stabilizers in their corresponding ExStabilizer(Au-Citr)/SiO₂ samples. This is in line with the interaction of the Citr stabilizer with the Au NPs which was significantly weaker than the other stabilizers (PVP, PVA and CTAB).^{6,12–15}

Given in Table 1 are the catalytic data of p-CNB hydrogenation on Au-Citr/SiO2 and ExStabilizer(Au-Citr)/SiO2 catalysts; the conversion level of p-CNB was controlled at lower than 30% for a more reliable comparison of the Au activity. p-Chloroaniline (p-CAN) was detected as the sole product according to GC analysis, which is consistent with earlier studies on hydrogenation of nitro-aromatics over Au catalysts on various supporting oxides.^{19,24} The rate of *p*-CNB consumption was normalized according to the Au mass and number of surface Au atoms, respectively, to measure the Au mass-specific activity (MSA, mol $h^{-1} g_{Au}^{-1}$) and turn-over frequency of p-CNB (TOF_{p-CNB}, h^{-1}) over the surface Au atoms. Both the MSA_{Au} and TOF_{p-CNB} numbers for the ExPVP(Au-Citr)/SiO₂ and ExPVA(Au-Citr)/SiO₂ samples were significantly higher than those for the Au-Citr/SiO₂ and ExCTAB(Au-Citr)/SiO₂ samples. The fact that the differences in TOF_{p-CNB} between the two former catalysts and the latter two were not proportional to their variations in MSA_{Au} would be due to the unavoidable Au growth during the immobilization of Au-Citr NPs or during the exchange of Au-Citr with CTAB and the following up immobilization of ExCTAB(Au-Citr) (Fig. 3 and 4). The lowering by 3-4 folds in the Au activity by TOF_{p-CNB} for Au-Citr/SiO₂ (71 h⁻¹) and ExCTAB(Au-Citr)/SiO₂ (47 h^{-1}) compared to those for ExPVP(Au-Citr)/SiO₂ (182 h⁻¹) and ExPVA(Au-Citr)/SiO₂ (220 h⁻¹) clearly indicates that the intrinsic catalytic activity of Au NPs for p-CNB hydrogenation depended sensitively on the nature of their stabilizer. Thus, the polymeric stabilizers (PVP and PVA) served as very efficient activity promoters to their stabilized catalytic Au NPs, which suggests that steric blocking of the active Au sites by these polymers is of little importance to the hydrogenation reaction of p-CNB.

Promotion by PVA and PVP polymers of the Au activity for *p*-CNB hydrogenation becomes even more prominent when one compares the TOF_{*p*-CNB} numbers for Au-PVP/SiO₂ (218 h⁻¹) and Au-PVA/SiO₂ (260 h⁻¹) samples, which are presented in the lower part of Table 1. The Au TOF_{*p*-CNB} for ExCitr(Au-PVP)/SiO₂ (150 h⁻¹) and ExCitr(Au-PVA)/SiO₂ (161 h⁻¹) were *ca.* 30% lower than those for their corresponding Au-PVP/SiO₂ (218 h⁻¹) and Au-PVA/SiO₂ (260 h⁻¹) but still significantly higher than that for Au-Citr/SiO₂ (71 h⁻¹). These data may suggest that small percentages of the polymer stabilizer in Au-PVP and Au-PVA were indeed substituted by Citr during the stabilizer-substitution process though Citr is a weaker stabilizer than PVA and PVP and the substitution was not detected by UV-vis spectroscopy (*e.g.*, Fig. 2D). Difference between the two polymer stabilizers (PVP and PVA)

Table 2Catalytic data for Au NPs in ExStabilizer(Au-Citr)/SiO2 samples for theCAL hydrogenation reaction^a



	CAL	Product sel. (%)			MSA _{Au}			
Catalyst	conv. (%)	HCAL	COL	HCOL	$(\operatorname{mol}_{\operatorname{Au}}^{-1})$	$\begin{array}{c} \text{TOF}_{\text{CAL}} \\ \left(h^{-1} \right) \end{array}$		
Au-Citr/SiO ₂	5.8	72	20	7	0.12	263		
ExPVP(Au-Citr)/SiO ₂	8.6	72	23	5	0.17	168		
ExPVA(Au-Citr)/SiO ₂	11.0	76	20	4	0.22	215		
ExCTAB(Au-Citr)/SiO ₂	3.0	72	16	12	0.06	104		
^a Rxn conditions: 50 mg catalyst, 4 mmol CAL, 5 mL <i>p</i> -xylene (solvent).								

" Rxn conditions: 50 mg catalyst, 4 mmol CAL, 5 mL *p*-xylene (solvent), $P_{H_2} = 2$ MPa, 150 °C, 4 h. CAL/Au (molar) = 1600.

is also revealed in Table 1; the Au activity in Au-PVP/SiO₂ was clearly lower than that in Au-PVA/SiO₂, indicating that PVA is the stronger activity promoter to Au NPs.

Table 2 presents the catalytic results of Au-Citr/SiO₂ and ExStabilizer(Au-Citr)/SiO₂ for the hydrogenation of CAL. Hydrocinnamaldehyde (HCAL), cinnamyl alcohol (COL) and hydrocinnamyl alcohol (HCOL) were detected as the products produced by hydrogenation at the C=C, C=O and both C=C and C=O bonds, respectively. The ExPVA(Au-Citr)/SiO₂ catalyst produced the highest MSA_{Au} (0.22 mol h^{-1}_{1} $g_{Au}^{-1}_{1}$), followed by ExPVP(Au-Citr)/SiO₂ (0.17 mol h^{-1} g_{Au}^{-1}), Au-Citr/SiO₂ (0.12 mol h⁻¹ g_{Au}⁻¹) and ExCTAB(Au-Citr)/SiO₂ (0.06 mol $h^{-1} g_{Au}^{-1}$). However, the TOF_{CAL} data showed a different order: Au-Citr/SiO₂ (263 h^{-1}) > ExPVA(Au-Citr)/SiO₂ $(215 h^{-1}) > ExPVP(Au-Citr)/SiO_2 (170 h^{-1}) > ExCTAB(Au-Citr)/SiO_2$ $(104 h^{-1})$; the active sites associated with the larger Au NPs in the Au-Citr/SiO₂ catalyst (11.6 \pm 6.5 nm) appeared to be the most active but those on ExCTAB(Au-Citr)/SiO₂ (8.9 \pm 2.9 nm) the least active. In contrast to these consequences of the stabilizer exchanges on the catalytic TOF_{CAL} of Au, the product selectivity of CAL hydrogenation appeared not sensitive to the stabilizer exchange. The major product was HCAL (ca. 72%) from the selective hydrogenation at the C=C bond, irrespective of the stabilizer exchanges (Table 2). This observation is consistent with earlier studies on the hydrogenation of $\alpha,\beta\text{-unsaturated}$ aldehydes over Au/SiO $_2$ catalyst. 18,20,25,26

The differences in structure and polarity of the varying stabilizers, and their modification of the surface electronic property of Au NPs would be responsible for the above described effects of stabilizer exchange on the hydrogenation catalysis of Au NPs. The polymer stabilizers with polarizable groups (like C==O in PVP and OH in PVA) would form around Au NPs a dynamic and loosely organized organic layer that could cause steric hindrance and/or disturbance to the electronic structure of the catalytic Au sites. Our observations that both PVP and PVA stabilizers functioned as very efficient "promoters" for their stabilized catalytic Au NPs in the hydrogenation of *p*-CNB (Table 1) would suggest that steric hindering of the active Au sites by these polymers was of little importance to the hydrogenation of p-CNB. Similar product selectivity data in the hydrogenation of CAL (Table 2) would also demonstrate an insignificant steric hindering effect of the PVP and PVA stabilizers to the hydrogenation of α , β -unsaturated aldehydes. Electronic modification of the catalytic Au surface arising from the ligand effect of PVA and PVP could thus be responsible for the observed variation in the Au activity. According to the XPS^{5,8} and XANES⁸ measurements, and FTIR study of adsorbed CO,8 PVP-stabilized Au NPs would be electron-rich or more or less anionic^{5,8} while their PVA-stabilized counterparts could be neutral.^{5,18} It was shown that H₂ activation by dissociative adsorption would become more favorable on the neutral Au NPs than on their anionic counterparts.^{27,28} This would explain why ExPVA(Au-Citr)/SiO₂ appeared more active for both reactions than ExPVP(Au-Citr)/SiO₂ (Tables 1 and 2). On the other hand, the ionic CTAB stabilizer would be inclined to assemble at the surface of Au NPs in the non-polar solvent of the hydrogenation reactions (toluene or p-xylene), forming a relatively dense cationic CTA-layer around the Au NPs²⁹ and imposing a severe block to the accessibility of the catalytic Au sites for p-CNB and CAL molecules. This could be responsible for the very low TOF_{p-CNB} and TOF_{CAL} numbers of the ExCTAB(Au-Citr)/SiO₂ catalyst for the hydrogenation reactions. These explanations are in line with Quintanilla et al.,9 who reported that PVP could wind around Au NPs to form a kind of "Au-core@porous-PVP-shell" architecture while dodecylamine would form on the Au surface a close-packed self-assembled layer, which imposed a severe block to the catalytic Au sites for the oxidation of benzyl alcohol in toluene (solvent).

The TOF numbers over the Au NPs in Au-Citr/SiO₂ catalyst, high TOF_{CAL} and low TOF_{p-CNB} , were distinctly different for the two hydrogenation reactions. The low TOF_{p-CNB} could arise from blocking of and/or electronic modification of the active Au sites due to the adsorption of citrate anions even although the amount of Citr stabilizer would be low in this Au-Citr/SiO₂ sample, as indicated by its IR spectrum (Fig. 5). The unexpectedly high TOF_{CAL} number (the highest among all of the four catalysts) would suggest that the active Au sites for the two hydrogenation reactions were not identical, even if they were not quite different, over this Au-Citr/SiO₂ catalyst. It was shown that H₂ activation by dissociative adsorption could be the rate determining step for the hydrogenation of p-CNB over nanosized Au catalysts on various oxide supports.^{19,24} The contrastingly high TOF_{CAL} and low TOF_{p-CNB} numbers of the Au-Citr/SiO₂ catalyst would suggest a different rate determining step in the hydrogenation of CAL, probably a Langmuir-Hinshelwood type surface reaction (step) between adsorbed CAL and its neighboring H atoms (from H2 activation).²⁰ The Citr stabilizer in this Au-Citr/SiO₂ catalyst could be "bifunctional", in that it blocked some Au sites for H₂ activation but at the same time subtly modified the electronic

property of Au NPs to favor CAL adsorption and activation. Also, the significantly larger Au sizes (11.6 \pm 6.5 nm) of the Au-Citr/SiO₂ sample would mean more or less Citr redistribution on these enlarged Au particles, which offered more open Au surface and possibly more specific sites in favor of CAL activation. All these factors would contribute to maintain a balanced activation of both H₂ and CAL, making the catalytic sites in this Au-Citr/SiO₂ specific and much more active for CAL hydrogenation.

4. Conclusions

This work demonstrates that citrate anion was a weak stabilizer for Au NPs in the colloidal solution and can be easily substituted with PVP, PVA and CTAB, respectively. The substitution with the polymer stabilizers (PVP and PVA) showed not only no impact on the Au size in the colloidal solution but also "prevented" possible growth of the Au NPs during their immobilization on the non-interacting SiO₂ support. CTAB appeared to be a relatively weaker stabilizer; its exchange with Au-Citr was accompanied by significant enlargement of the Au NPs. These stabilizer substitutions produced significant impact on the catalysis of Au NPs for the hydrogenation of both p-CNB and CAL, due to steric hindrance or electronic modification, or both of the two effects imposed upon by the different stabilizers. The distinctively varied Au activity of the Au-Citr/SiO₂ catalyst in the two hydrogenation reactions would imply that the active Au sites for CAL activation were different from those for *p*-CNB activation.

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