

Immobilization of polymer-stabilized metal colloids by a modified coordination capture: preparation of supported metal colloids with singular catalytic properties

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Received 19 May 1998; accepted 4 August 1998

Abstract

Polymer-stabilized metal colloids interact with various supports which have been pretreated with ethanol solution of triphenylphosphine (TPP), then the polymer and TPP are washed off with H₂O and toluene/EtOH solvents sequentially, to give the supported metal colloids with the same size and size distribution as their precursor. The as-prepared supported platinum colloids exhibit superior catalytic properties to their precursor in selective hydrogenations of *o*-chloronitrobenzene to *o*-chloroaniline and citronellal to citronellol. This reveals the great potentiality of nanoscale metal colloids in catalysis. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Immobilization; Coordination; Colloid; Catalysis

1. Introduction

Metal nanoclusters or colloids with size of 1–10 nm are very important [1–10]. In recent years, many papers have been published on the quantum effect [11], magnetism [12], electronics [13] and catalysis [1–10,14] of these colloids. Although colloids dispersed in solution displayed novel catalytic properties in many reactions, it is still necessary to immobilize them on

various supports in view of practical application. Some researchers have immobilized the ligand-stabilized colloidal Pd, Ni, Ag and Ir₄, Ir₆ clusters on different supports (Al₂O₃, SiO₂, MgO and NaY zeolite), respectively [15–21]. As far as polymer-stabilized metal colloids, several ways have also been proposed to solve this problem, such as the formation of polyion complex between poly(acrylic acid) (stabilizing polymer) and poly(ethyleneimine) [22], the cross-linking reaction between acrylate- or acrylamide-containing stabilizing copolymer and poly(acrylamide) gel [23] and the electrostatic adsorption of metal colloids onto the ion-ex-

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change resin [24]. Liu et al. investigated several other methods: (1) formation of polymer hydrogen-bonding complex between poly(acrylic acid) and stabilizing polymers (e.g., poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(vinyl alcohol)) [25]; (2) utilization of the functional groups (e.g., hydroxyl group) on the silica surface to immobilize the polymer-stabilized metal colloids by addition of organic acids [26]; and (3) capture of colloidal metal particles onto the surface of functionalized silica by ligand coordination—named as ‘coordination capture’ [27,28]. The coordination capture is a method to immobilize metal colloids, but it also provides a useful way to prepare XPS specimens for polymer-stabilized metal colloids, because the polymer covers the colloidal particles and prevents the photoelectron emission whilst a large part of the stabilizing polymer can be get rid of by this way [29].

Owing to the high dispersity, many of the supported metal colloids displayed higher reactivity than the conventional heterogeneous catalysts. However, there was no example of the immobilized metal colloids that are obviously superior to their precursors—the polymer-stabilized metal colloids dispersed in solution—in the catalytic activity and selectivity other than a recent paper reported by us [30], in which platinum nanoparticles were immobilized on the supports simply by the physical adsorption. However, this method was limited by the adsorption properties of the supports to metal particles, and the content of adsorbed metal is low and hard to be controlled. By improving the coordination capture through the removal of the ligand and all the residual polymer, there will be the wholly naked nanosized platinum colloidal particles on supports. Here, we describe a ‘modified coordination capture’ method to quantitatively immobilize the PVP-stabilized metal colloids and report the unusual performances of the as-prepared supported platinum colloids in the selective hydrogenations of *o*-chloronitrobenzene (**1**) to *o*-chloroaniline (**2**) and citronellal (3,7-dimethyl-6-octenal) (**3**) to

citronellol (3,7-dimethyl-6-octene-1-ol) (**4**). These results may disclose the inherent excellent properties of metal colloids.

2. Experimental

2.1. Materials and instruments

PVP (average molecular weight 40 000) was supplied by BASF. Other reagents were purchased from Beijing Chemicals and had a level of analytical grade. **1** was recrystallized in 95% ethanol before use. Hydrogen (H₂) with a purity of 99.999% was supplied by Beijing Gases Factory.

Poly(styrene-co-divinylbenzene) beads (PS) was thoroughly treated according to the reference procedure [31]. Elemental analysis showed that all the inorganic and organic additives did not exist (Calculated: C, 92.25; H, 7.75; N, 0. Found: C, 92.12; H, 7.84; N, 0). The surface area of PS was 340 m² g⁻¹. Other supports, Al₂O₃ and MgO with surface area of 16.8 and 56.9 m² g⁻¹, respectively, were used as purchased.

Transmission electron microscopy (TEM) photographs were taken by using a Hitachi-9000NAR instrument. Specimens were prepared by placing a drop of the colloid solution or solid suspension upon a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the enlarged photographs and the particle size distribution histograms were obtained on the basis of the measurements of about 300 particles. The hydrogenation products were analyzed by a Beifen Model SQ-204 gas chromatography.

2.2. Preparation of supported metal colloids

Colloidal platinum, stabilized by PVP (M.W. = 40 000), were prepared by the reported method [32] as a dark-brown homogeneous dispersion (designated as PVP-Pt, and the molar

ratio of monomeric unit of PVP to platinum, PVP: Pt = 50).

The supported platinum colloids were prepared as follows (all the procedures were carried out at room temperature). In a 50 ml flask, 2.0 g support (PS, Al₂O₃ or MgO) was stirred with 0.11 g TPP dissolved in a suitable amount of EtOH for 3 h, and was dried by rotatory evaporation. Then, 12.5 ml PVP-Pt colloidal dispersion (containing Pt 7.60×10^{-5} mol) was added and stirred with the support for 24 h. After filtration, the support was firstly extracted in a Soxhlet extractor with H₂O for 48 h, and toluene/EtOH (4:1) mixed solvents for 48 h, secondly, then dried under vacuum for 5 h to give the supported platinum colloids—Pt/PS, Pt/Al₂O₃ or Pt/MgO. The content of platinum was about 0.5–1% by weight determined by UV-VIS spectrometry [33]. Elemental analysis showed that N=0 which indicated that the stabilizing polymer, PVP, was washed off. To metal oxide supports, elemental analysis showed that C=0 and H=0, which indicated that TPP was washed off, too. Other metal colloids, PVP-Pd, PVP-Rh, PVP-Ir (prepared as literature [32]) and PVP-Ru [34] were also immobilized by this way on PS, Al₂O₃ and MgO, respectively.

2.3. Hydrogenation reaction

Selective hydrogenation of **1** to **2** was carried out at 303 K and atmospheric pressure. In a two-necked flask equipped with a magnetic stirrer and a thermostatic water bath, there were placed about 0.1 g platinum/support catalyst (containing Pt 2.60×10^{-6} mol), 0.10 ml *n*-C₁₄H₃₀ (as internal standard for gas chromatography) and 13.9 ml MeOH. H₂ was charged several times to replace air and the catalyst was activated at 303 K for 60 min. After 1.00 ml **1**/MeOH solution (containing **1** 7.50×10^{-4} mol) was injected into the flask, the reaction started. The hydrogen consumption was monitored with a graduated gas burette. When the volume of the theoretical uptake of H₂ was reached, the reaction was stopped and the reac-

tion solution was analysed by gas chromatography. When using PVP-Pt as the catalyst, the reaction solution contained 2.60×10^{-6} mol Pt, 1.30×10^{-4} mol (monomeric unit) PVP; the others were the same as described above.

Selective hydrogenation of **3** to **4** was carried out in a 100 ml stainless-steel autoclave. The reaction solution contained 25 ml EtOH, 5 ml H₂O, 0.10 mg NaOH, 0.500 g **3** (3.24×10^{-3} mol), 1.00 g ethylene glycol (as an internal standard for gas chromatography) and about 0.1 g supported platinum catalysts (containing 2.30×10^{-6} mol Pt). H₂ was charged several times to replace air and the final pressure of H₂ was 6.0 MPa. The hydrogenation reaction was performed at 333 K for 2 h. The reaction products were analyzed by gas chromatography. When using PVP-Pt as the catalyst, the reaction solution contained 2.30×10^{-6} mol Pt with 1.15×10^{-4} mol (as monomeric unit) PVP.

3. Results and discussion

3.1. Characterization of PVP-stabilized and the supported metal colloids

PVP-Pt and the supported Pt colloids were characterized by TEM. TEM images showed that the mean diameter of PVP-Pt was 1.12 nm with a narrow size distribution in the range of 0.6–1.8 nm with $\sigma = 0.30$ nm (Fig. 1).

The particle diameters and size distributions of Pt/PS and Pt/Al₂O₃ measured from the enlarged TEM photographs were 1.14 nm ($\sigma = 0.31$ nm) and 1.13 nm ($\sigma = 0.31$ nm), respectively (Fig. 2). This result declared that the supported Pt colloids had the same size and size distribution as their precursor—PVP-Pt. Other supported metal colloids gave the same results, too. For example, the average diameters and the standard deviations of PVP-Ru, Ru/Al₂O₃ and Ru/MgO were 1.38 nm ($\sigma = 0.51$ nm), 1.41 nm ($\sigma = 0.54$ nm) and 1.32 nm ($\sigma = 0.45$ nm), respectively. It should be noted that few papers described the formation of Ru colloids. Bradley

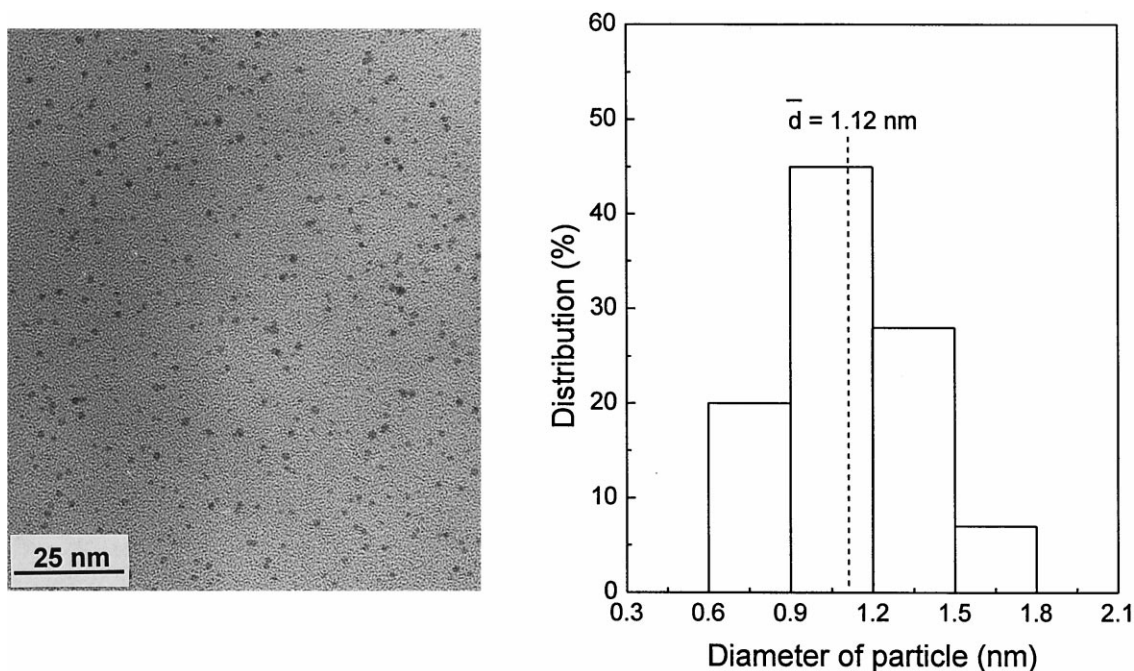


Fig. 1. Electromicroscopic photograph (left) and the corresponding particle size histogram (right) of PVP-Pt colloid.

et al. [35] synthesized nitrocellulose- and cellulose acetate-stabilized Ru colloids via dihydrogen dissociation of $\text{Ru}(\text{cod})(\text{cot})$ (cod = cyclooctadiene, cot = cyclooctatriene) in organic solvents. Bönemann et al. [3] prepared tetraalkylammonium-stabilized Ru colloids by hydrotriorganoborate reduction. We [34] employed NaBH_4 to reduce $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in the presence of PVP to obtain the PVP-Ru dispersed in $\text{MeOH-H}_2\text{O}$ mixed solutions, which were characterized by TEM and XPS (X-ray photoelectron spectra). Using PVP-Ru as a catalyst, *o*-chloronitrobenzene can be selectively hydrogenated to *o*-chloroaniline with 100% selectivity at 100% conversion [36] and citronellal to citronellol with 95.2% selectivity at 88.4% conversion [37]. And here for clearance, a TEM photograph of PVP-Ru was shown in Fig. 3.

3.2. Preparation of supported metal colloids by the modified coordination capture

The catalytic properties of supported metal catalysts are mainly relevant to the following

aspects to a given metal: (1) size, size distribution and surface geometry of metal particles; (2) influence of additives; and (3) metal-support interaction or support effect. It is difficult to obtain the same dispersion and surface geometry for metal catalysts from the same precursor but on different supports by conventional methods [38].

Coordination capture [27,28] is an effective method to immobilization polymer-stabilized metal colloids (Scheme 1). However, it suffers from the need for a series of complicated steps to prepare the functionalized support and retains many strong coordination ligands (e.g., mercapto group) which are not good for the catalytic properties of platinum group metals. The modified coordination capture uses TPP instead of strong coordination ligand-containing compounds to quantitatively 'capture' the metal colloidal particles from solution, then gets rid of TPP to eliminate its effect (e.g., toxication) to metal catalysts. So, this method will provide a more active catalyst than before. The process can be schematically shown as Scheme 2.

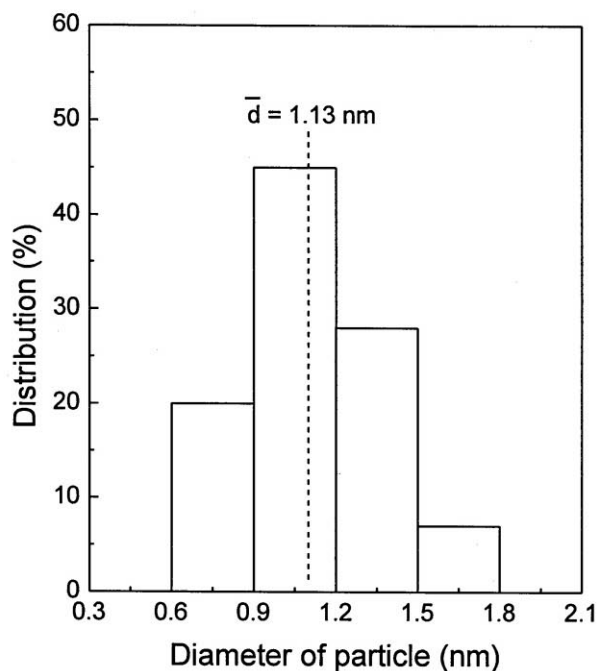
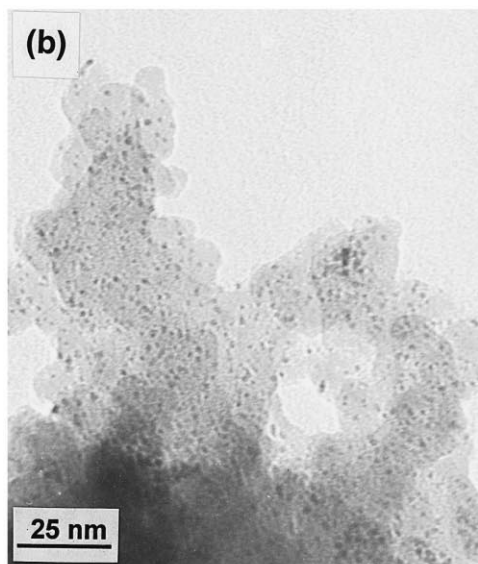
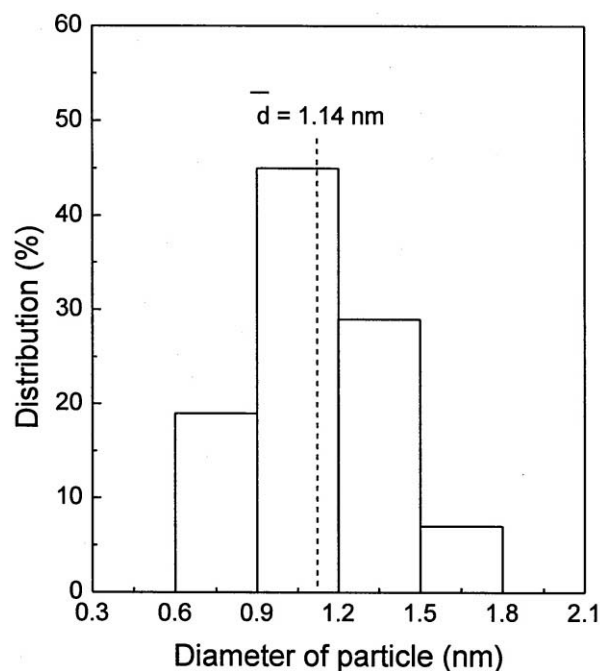
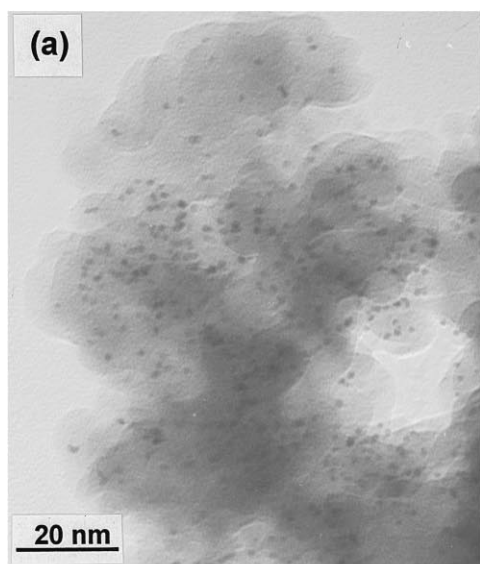


Fig. 2. Electromicroscopic photographs (left) and the corresponding particle size histograms (right) of (a) Pt/PS and (b) Pt/Al₂O₃.

From Scheme 2, it is easy to understand why there are two steps of extraction in preparation. The first step is to remove the stabilizing poly-

mer, PVP, and leave metal colloidal particles on the surface of support. The second step is to remove the coated ligand, TPP. Besides TPP,

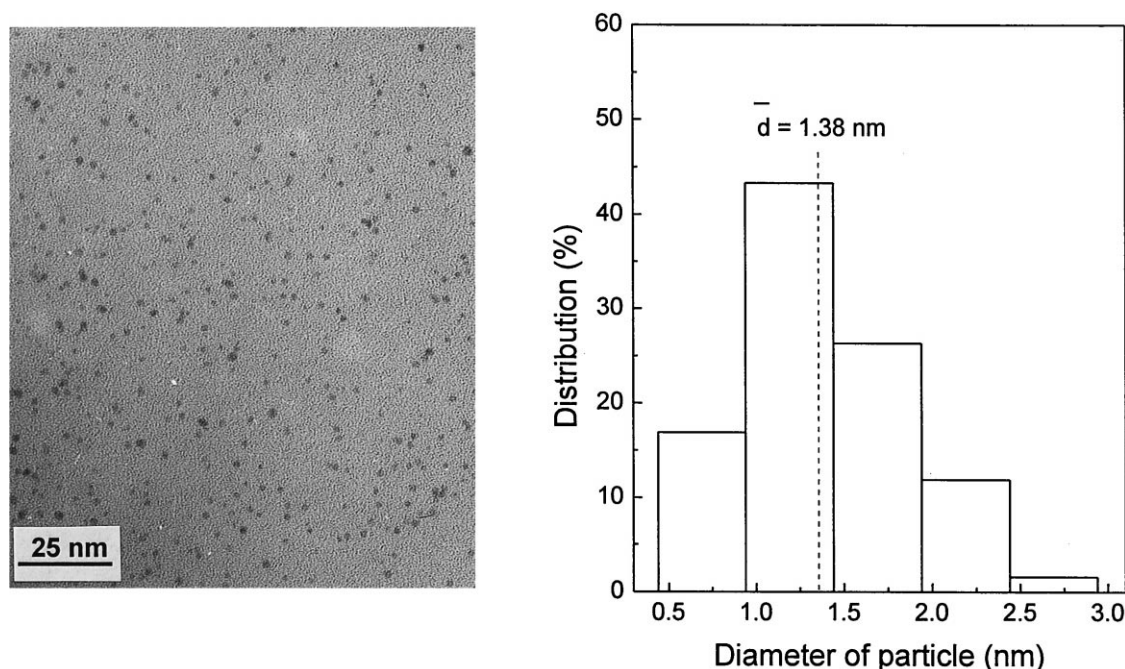
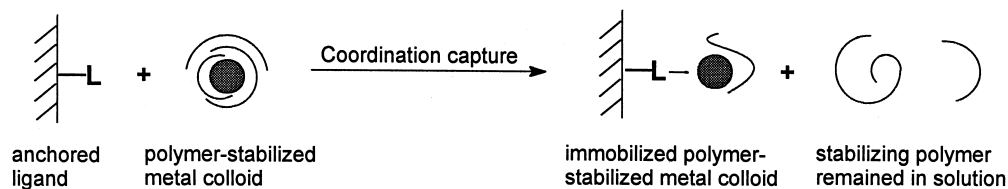


Fig. 3. Electromicroscopic photograph (left) and the corresponding particle size histogram (right) of PVP-Ru colloid.

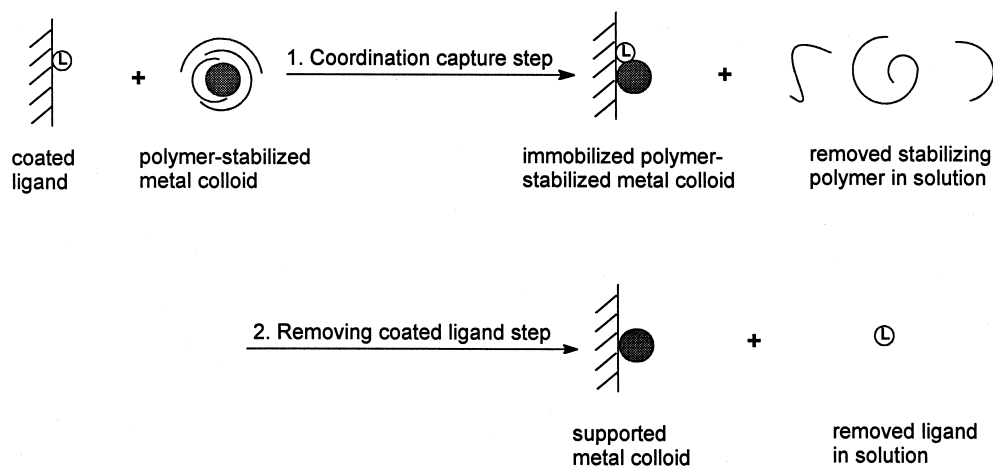
any ligand which has different solubility from the stabilizing polymer can be used in this method. Another example is 8-hydroxyl quinine. Table 1 listed some supported metal colloids prepared by this method.

Comparing the supported metal colloids with their precursor—PVP-stabilized metal colloids, these catalysts had the same mean diameter and the same narrow size distribution (1.1 nm and $\sigma = 0.3$ nm for platinum colloids) demonstrated by the TEM observation. This was also verified by our previous works on the immobilization of PVP-Pd by formation of polymer hydrogen bond

complexes [25] and the coordination capture [27,28]. The metal-support interactions may induce some special particles morphologies through high-temperature reduction, but this method was conducted at room temperature, therefore, the possibility of changes in morphologies of platinum colloidal particles was very remote. It can be assumed that the colloidal particles of these catalysts had the same surface geometry. Atomic absorption spectrometry and elemental analysis results indicated that there was no other residual components (in this work, it was Na^+ , Cl^- and PVP). Thus, to this



Scheme 1. Coordination capture.



Scheme 2. Modified coordination capture.

method, the forenamed two influences, (1) and (2), were excluded. But there still may be some subtle changes in morphology, and few residues which were not detected by conventional instruments. Anyhow, we got the same size, size distribution and surface geometry for metal catalysts from the same precursor but on different supports. As a result, the exhibited different catalytic properties of supported metal colloids were ascribed to the metal-support interactions or support effects. Furthermore, the modified coordination capture provides an effective

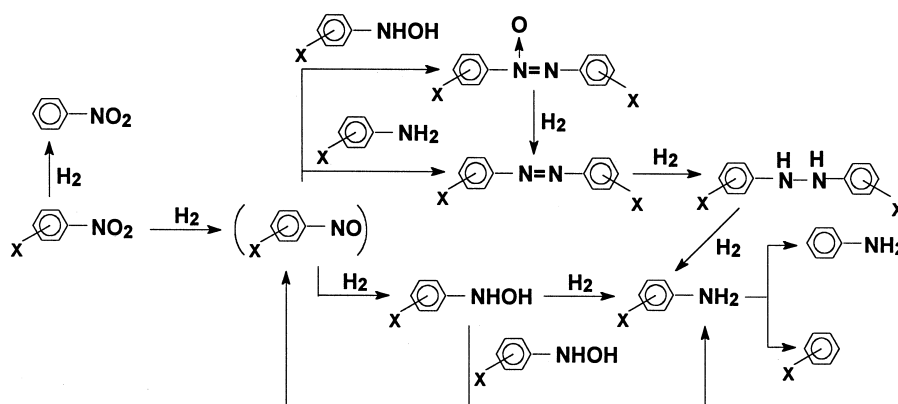
method to control the particle size and size distribution of supported catalysts, and remain their nascent catalytic properties [39]. In the following text, we investigate the different catalytic properties of PVP-Pt and the supported Pt colloids in two reaction systems.

3.3. Selective hydrogenation of **1** to **2**

Aromatic haloamines are important materials in the chemistry of pesticides and herbicides. The process of hydrogenation of **1** is very com-

Table 1
Preparation of supported metal colloids by the modified coordination capture

Precursor	Ligand	Supported metal colloid	Content of metal (wt. %)
PVP-Pt	TPP	Pt/PS	0.50
	TPP	Pt/Al ₂ O ₃	0.5–1.3
	TPP	Pt/MgO	0.5–1.0
	8-hydroxyl quinoline	Pt/Al ₂ O ₃	0.50
	8-hydroxyl quinoline	Pt/MgO	0.50
PVP-Pd	TPP	Pd/PS	0.50
	TPP	Pd/Al ₂ O ₃	0.50
	TPP	Pd/MgO	0.50
PVP-Rh	TPP	Rh/Al ₂ O ₃	0.50
PVP-Ir	TPP	Ir/Al ₂ O ₃	0.50
PVP-Ru	TPP	Ru/PS	0.50
	TPP	Ru/Al ₂ O ₃	0.50
	TPP	Ru/MgO	0.50



Scheme 3. Reaction pathway of hydrogenation of halogenated nitrobenzene.

plicated and it will give many products: *o*-chloroaniline (**2**), nitrobenzene (**5**), aniline (**6**), *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, azo- and azoxy-dichlorobenzenes, chlorobenzene, and so on (Scheme 3).

Metal colloids dispersed in solution have to be stabilized by various ligands or polymers, e.g., PVP. The supports can also be looked upon as a kind of ligand which stabilize the supported metal colloidal particles. It is obvious that the number of the contact sites between support and metal particles in metal/support is

much fewer than that in the PVP-Pt. Considering that a lot of active sites of PVP-Pt are encapsulated by PVP, the supported naked platinum colloids will exhibit higher activity. The experiment confirmed this assumption: the activity of the neat PVP-Pt colloid was much lower than those of supported platinum colloid catalysts (0.69 and about $1.0 \text{ mol H}_2 \text{ (mol Pt} \cdot \text{s)}^{-1}$, respectively) (see Table 2 and Fig. 4).

Moreover, it also can be found from Table 2 that PVP-Pt displayed inferior selectivity for **2** to platinum/support (60% and about 80%, re-

Table 2

Hydrogenation of **1** to **2** over the PVP-Pt and the supported platinum colloid catalysts^a

Catalytic system	Initial rate (mol H ₂ /mol Pt · s)	Average rate ^b (mol H ₂ /mol Pt · s)	Selectivity ^c (%)			
			2	5	6	Others
PVP-Pt	1.90	0.690	60.2	1.2	0.9	37.7
Pt/PS	3.38	0.760	81.9	1.3	11.1	5.7
Pt/Al ₂ O ₃	2.04	1.00	79.9	9.3	7.7	3.1
Pt/PS-PVP	2.25	0.600	72.6	4.8	4.4	18.2
Pt/Al ₂ O ₃ -PVP	1.69	0.347	74.6	9.4	5.9	10.1
Pt/PS-NMP (1) ^d	2.95	0.663	76.4	5.3	11.5	6.8
Pt/PS-NMP (10) ^d	2.05	0.520	71.5	6.4	11.1	11.0
Pt/PS-NMP (50) ^d	1.95	0.498	68.6	5.1	11.6	14.7
Pt/PS-PVP ^e	2.77	0.623	74.2	5.9	11.5	8.4

^aReaction condition: **1** 7.50×10^{-4} mol, *n*-C₁₄H₃₀ 0.10 ml, Pt 2.60×10^{-6} mol, MeOH 14.9 ml, 303 K and 0.1 MPa.

^bCalculated at 100% conversion of **1**.

^cObtained at 100% conversion of **1**; **5** = nitrobenzene, **6** = aniline, Others = *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

^dThe numbers in the brackets refer to the molar ratio of NMP:Pt.

^eThe average molecular weight of PVP used here was 360 000.

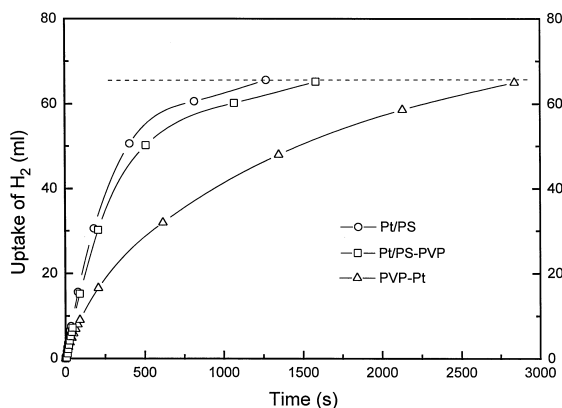


Fig. 4. Time courses of the hydrogenation of **1** catalyzed by PVP-Pt, Pt/PS and Pt/PS-PVP catalytic systems.

spectively). This indicated that PVP was harmful to not only the activity but also the selectivity. The data of Pt/PS-PVP and Pt/Al₂O₃-PVP were consistent with this assumption (here, the molar ratio of PVP:Pt was 50:1). PVP is a polymer which has an average molecular weight of 40 000. It usually contacts with metal particles in the form of loop, and there are much fewer chain segments to join in the modification for the reason of steric hindrance in the supported catalyst's system. But a small molecule can contact with metal particles freely. If we choose a small molecule with the same functional structure instead of PVP to participate in the reaction, the activity will decrease much more, so does the selectivity. To prove the validity of this idea, *N*-methylpyrrolidone (NMP, M.W. = 99.13) was selected. When the molar ratio of NMP:Pt increased from 1:1 to 50:1, the activity and selectivity to **2** for Pt/PS-NMP decreased consequently (from 2.95 to 1.95 mol H₂ (mol Pt · s)⁻¹ and from 76.4% to 68.6%). At the same molar ratio of NMP:Pt and PVP: Pt (50:1), NMP influenced much more than PVP. Identically, using PVP with M.W. = 360 000, it can be expected that Pt/PS-PVP (360 000) will exhibit higher activity and selectivity than Pt/PS-PVP (40 000). The results from Table 2 agreed with this inference.

PS is easily available and is widely applied in gas chromatography (as a stationary phase) and

ion exchange resin, etc. But it contains many inorganic and organic additives (e.g., CaCO₃, surfactants, etc.) in the stage of manufacture. This is disadvantageous for a catalyst support. After getting rid of those additives, it is only composed of carbon and hydrogen. Therefore, PS can be employed as a pure and inert support distinguished from others. The differences of Pt/PS and Pt/Al₂O₃ in catalytic properties, though it is not clear at present, may be ascribed to the different characteristics of the supports.

All the as-prepared supported metal colloid catalysts can be recovered by filtration and rinsing. The recovered catalysts displayed near the same activity and selectivity as the originals (see Fig. 5). The above results disclose the inherent excellent properties of metal colloids.

3.4. Selective hydrogenation of **3** to **4**

3 and **4** are non-conjugated unsaturated aldehyde and unsaturated alcohol. To obtain **4** by selective hydrogenation of **3** is an important work [40–42]. There are two competitive hydrogenation reactions starting from **3** (Scheme 4).

Table 3 shows the catalytic results of different catalysts. Catalyzed by PVP-Pt, the conversion of **3** was just 70.6% with 44.5% selectivity to **4**. When using supported platinum colloids as the catalysts, both the conversion and the selectivity increased to about 80–90%. From Fig. 6, it can be seen that the yield of **4** reached 88.5%

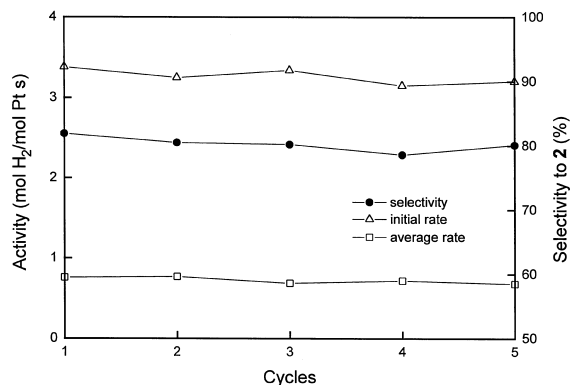
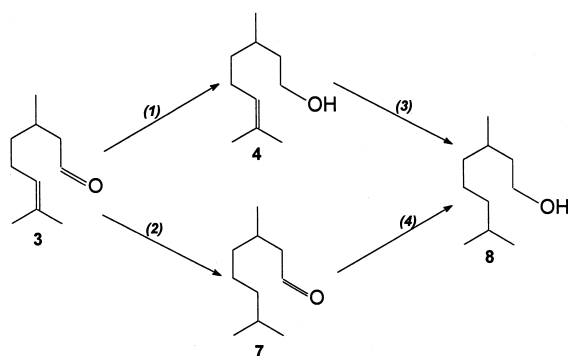


Fig. 5. Catalytic properties of Pt/PS after recycling.

Scheme 4. Reaction pathway of hydrogenation of **3**.

at 94.0% conversion of **3** in 60 min (selectivity 94.1%). And the selectivity decreased from 94.1% to 81.2% and the by-product **8** reached 18.8% in another 60 min. This result made an important step to the goal of the research proposed by Boudart [41]: to get unsaturated alcohols from unsaturated aldehydes with high selectivity by nanocluster catalysis.

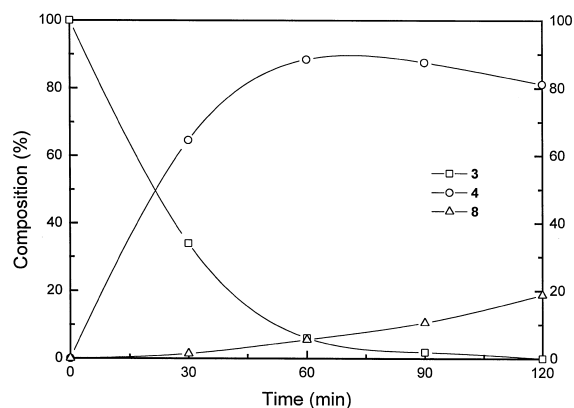
Although the interaction of PVP with metal colloidal particles is weak, the influence of PVP to the catalytic properties of Pt colloids on steric or electronic aspects could not be neglected. PVP interacts with noble metal colloidal particles weakly by its C=O group's coordination [5], the active sites on the surface of Pt particles for hydrogenation of C=O double bond in the molecule of **3** were partially occupied by the competitive adsorption of PVP; consequently, the activity and the selectivity of Pt/PS were

Table 3
Hydrogenation of **3** to **4** over the PVP-Pt and the supported platinum colloid catalysts^a

Catalyst	Conversion of 3 (%)	Selectivity ^b (%)	
		4	8
PVP-Pt	70.6	44.5	46.0
Pt/PS	100.0	81.2	18.8
Pt/Al ₂ O ₃	95.5	92.8	7.2

^aReaction condition: **3** 0.500 g (3.24×10^{-3} mol), ethylene glycol 1.00 g, Pt 2.30×10^{-6} mol, EtOH 25 ml, H₂O 5 ml, NaOH 0.10 mg, 333 K and 6.0 MPa, 2 h.

^bThe yield of **7** was under the detectable level of GC except PVP-Pt catalyst where the selectivity to **7** was 9.5%.

Fig. 6. Hydrogenation of **3** over Pt/PS.

higher than those of PVP-Pt. This has been proved in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol [30].

The above result is similar to that of the selective hydrogenation of **1** to **2**: the supported platinum colloids displayed superior catalytic properties to their precursor—the PVP-stabilized platinum colloid dispersed in solution. Both of these two types of selective hydrogenation reactions, of N=O and C=O double bonds, manifest that the nanosized metal colloids have much greater potential in catalysis. And the modified coordination capture is an effective approach to immobilize metal colloids with good catalytic performances.

4. Conclusions

(1) The modified coordination capture is a useful method to prepare supported metal colloids with the same size and size distribution as their precursor—the PVP-stabilized metal colloids dispersed in solution.

(2) The supported platinum colloids prepared by the modified coordination capture exhibited excellent catalytic properties in selective hydrogenation of N=O and C=O double bonds. This demonstrates the great potentiality of metal colloids in catalysis.

Acknowledgements

Financial support for this work by the National Science Foundation of China (Contract No. 29774037) and the Fund of the Chinese Academy of Sciences (Contract No. KJ952-J1-508) is gratefully acknowledged.

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