

Letter

Novel catalytic properties of supported metal nanoclusters

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Abstract

Nanosized platinum clusters were immobilized on different supports at room temperature. The supported clusters displayed novel catalytic properties compared to their precursor—polymer-stabilized colloidal platinum nanoclusters—in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol. This reveals the great potential of nanoscale metal clusters in catalysis. © 1998 Elsevier Science B.V.

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1. Introduction

Metal nanoclusters are very important in catalysis, and some papers have been published on the distinctive catalytic behaviors of nanoclusters dispersed in solution [1–12]. The ligand-stabilized metal clusters, however, are unstable in reaction even at ambient conditions. Thus, many researchers immobilized the metal nanoclusters on supports in view of its practical application. The groups of Turkevich and Kim [13], Reetz and Quaiser [14,15], Chao and Andres [16], Schmid et al. [17], Gates [18], and Xu et al. [19] have immobilized the ligand-stabilized colloidal Pd, Ni, Ag and Ir₄, Ir₆ clusters on different supports (Al₂O₃, MgO, SiO₂ and NaY zeolite), respectively. On the other hand, polymer-stabilized metal clusters are comparatively stable and can endure severe reaction

conditions, such as in the hydroformylation of propylene (4.0 MPa and 363 K) [20] and the carbonylation of methanol (3.0 MPa and 413 K) [21,22]. It offers a good opportunity to compare the catalytic performances of such ‘soluble’ metal clusters with the supported cluster catalysts derived from them. Several publications have reported the immobilization of the polymer-stabilized colloidal metal clusters [23–27]. Many of the supported metal nanoclusters displayed higher reactivity than the conventional heterogeneous catalysts. However, there was no evidence that the immobilized metal nanoclusters are obviously superior to their precursor—the polymer-stabilized metal clusters dispersed in solution—in their catalytic activities and selectivities. In the course of the study on the immobilization of nanoscale metal clusters, we found out that the poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized platinum colloidal clusters can be directly immobilized on supports without special treatment at about 0.5% loading. Hence,

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we got the wholly naked nanosized platinum colloidal clusters on supports, and they exhibited unusual performance in the selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) and other reactions. Here we will report the preliminary results.

2. Experimental

Colloidal platinum nanoclusters, stabilized by PVP (M.W. = 40 000), were prepared by the reported method [28] as a dark-brown homogeneous dispersion (designated as Pt–PVP; molar ratio of monomeric units of PVP to platinum, PVP:Pt = 50). TEM images showed that the mean diameter of Pt–PVP was 1.1 nm with a narrow size distribution in the range of 0.6–1.8 nm with $\sigma = 0.30$ nm.

Poly(styrene-co-divinylbenzene) porous beads (PS) were thoroughly washed according to the reference procedure [29]. Elemental analysis showed that all the inorganic and organic additives were washed out (Calculated: C, 92.25; H, 7.75; N, 0. Found: C, 92.12; H, 7.84; N, 0). The surface area of PS was $340 \text{ m}^2 \text{ g}^{-1}$. Other supports, MgO, TiO₂ and Al₂O₃ with surface areas of 56.9, 10.6 and $16.8 \text{ m}^2 \text{ g}^{-1}$, respectively, were used as purchased.

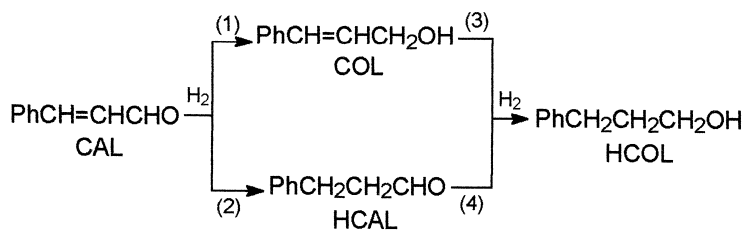
The supported platinum nanoclusters were prepared as follows. In a 50-ml flask, 1.0 g support was stirred with the required amount of Pt–PVP dispersion for 24 h at ambient temperature. After filtration, the support was extracted in a Soxhlet extractor with EtOH–H₂O (1:1) for 24 h, then dried at room temperature under vacuum for 5 h to give the supported platinum nanoclusters. The content of platinum was about 0.5% by weight (except for Pt/TiO₂, 0.22%) determined by UV–VIS spectrophotometry [30] and atomic absorption spectrometry. The particle diameters and size distribution measured from the enlarged TEM photographs were similar to that of Pt–PVP, i.e., 1.1 nm with $\sigma = 0.30$ nm. Elemental analysis showed that $N = 0$

which indicated that the stabilizing polymer, PVP, was thoroughly washed off.

Selective hydrogenation of CAL to COL was carried out in a 100-ml stainless-steel autoclave. The reaction solution contained 25 ml EtOH, 5 ml H₂O, 0.1 mg NaOH, 0.200 g CAL (1.51×10^{-3} mol), 0.200 g tetradecanol (as an internal standard for gas chromatography) and about 0.1 g supported platinum catalysts (containing 2.60×10^{-6} mol Pt). H₂ was charged several times to replace air and the final pressure of H₂ was 4.0 MPa. The hydrogenation reaction was performed at 333 K for 2 h. The reaction products were analysed by gas chromatography. When Pt–PVP was used as the catalyst, the reaction solution contained 2.60×10^{-6} mol Pt with 1.30×10^{-4} mol (as monomeric unit) PVP. The others were the same as stated above.

3. Discussion

Platinum has one more electrosphere than Pd, Rh, etc., so it is more easily polarized [27]. Consequently, it is easier for platinum to be immobilized on the supports through a physical interaction. The immobilized platinum nanoparticles had the same mean diameter and the same narrow size distribution; this was also in accord with our previous work on the immobilization of Pd–PVP by the formation of polymer hydrogen-bonding complexes and by coordination capture [25–27]. Furthermore, all the other residual components, such as ions (here, they were Na⁺ and Cl[−]), stabilizing polymer—PVP did not exist as verified by atomic absorption spectrometry and elemental analysis. In other words, we got the same size and size distribution for naked supported metal nanocluster catalysts from the PVP-stabilized platinum cluster. Now, Pt/PS can be used as a reference in which the metal clusters are immobilized on an inert support and the other supported catalysts can be compared with it. As a result, the exhibited different catalytic performances of the sup-



ported platinum nanoclusters are ascribed to the platinum nanoparticle-support interaction.

There are two competitive hydrogenation reactions starting from CAL (Scheme 1). Conventional heterogeneous catalysts can easily reduce the C=C double bond to yield hydrogenated cinnamaldehyde (HCAL) as the main product (Scheme 1, reaction (2)), but it is difficult to reduce the C=O double bond without reduction of the C=C double bond over monometallic platinum catalysts (Scheme 1, reaction (1)) [31].

To our surprise, when comparing the catalytic performances of Pt–PVP with those of Pt/PS, results were very different. A 37.5% conversion of CAL with 12% selectivity for COL was observed by using the polymer-stabilized metal cluster dispersion, Pt–PVP, as a catalyst. Under the same conditions, however, using the supported naked cluster, Pt/PS, as a catalyst more than doubled the catalyst's activity (79.7% conversion of CAL) and the selectivity for COL increased to 94.7% (Table 1).

Metal clusters dispersed in liquid medium are stabilized by various surfactants, ligands or

polymers. It is believed that the interaction of colloidal clusters with ligands greatly modifies the catalytic properties of the clusters. In the case of polymer-stabilized metal cluster dispersion, despite the relatively weak coordination ability of the stabilizing polymer (e.g., PVP) with the metal cluster, the polymer mantle surrounding the metal cluster will influence its catalytic properties to some extent. Modification of the polymer to the catalytic performances of the cluster could not be neglected. The supported platinum nanoclusters exhibited higher activity and selectivity; this indicated that PVP was harmful not only to the activity but also to the selectivity. To Pt–PVP, the stabilizing polymer, PVP, interacts with noble metal colloidal particles weakly by its C=O group's coordination [5]. The active sites on the surface of platinum nanoparticles for hydrogenation of C=O in the molecule of CAL were partially occupied by the competitive adsorption of PVP; consequently, the activity and the selectivity of Pt–PVP were lower than those of Pt/PS. To prove the validity of this hypothesis, PVP was

Table 1
Hydrogenation of CAL to COL over the Pt–PVP and the supported platinum nanocluster catalysts

Catalytic system	Conversion of CAL (%)	Average rate (mol H ₂ (mol Pt h) ⁻¹)	Selectivity ^a (%)		
			COL	HCAL	HCOL
Pt–PVP	37.5	84.2	12.0	80.0	8.0
Pt/PS	79.7	233.3	94.7	5.3	trace
Pt/MgO	61.5	180.0	97.1	2.9	trace
Pt/Al ₂ O ₃	53.5	156.6	76.6	23.4	trace
Pt/TiO ₂	57.0	166.8	70.3	29.7	trace
Pt/PS–PVP	69.9	204.3	92.1	7.9	trace
Pt/PS–NMP	50.3	147.3	66.0	34.0	trace

^aHCAL = hydrocinnamaldehyde, HCOL = 3-phenylpropan-1-ol.

introduced to the immobilized catalyst system. It can be seen from Table 1 that both the activity and selectivity of Pt/PS–PVP (molar ratio of PVP:Pt = 50) were slightly lower than those of Pt/PS. The steric hindrance of supports impedes the access of PVP to platinum particles; furthermore, many supports can adsorb PVP macromolecules [32,33]. All these factors make the influence of PVP on catalytic properties of platinum less vigorous in Pt/PS–PVP than in Pt–PVP. For the sake of reducing the steric hindrance of PVP macromolecule, we chose a small molecule with the same group structure instead of a macromolecule to participate in the reaction. When *N*-methylpyrrolidone (NMP) was added to the reaction system (NMP:Pt = 50), the reactivity of Pt/PS decreased from 204.3 to 147.3 mol H₂ (mol Pt h)⁻¹ and so did the selectivity to COL (from 92.1% to 66.0%) as compared to PVP. The above results on the influence of PVP and NMP just gave a partial explanation. The real reason why the naked platinum nanoparticles showed excellent properties when the PVP shell around the platinum nanoparticles was peeled off is not thoroughly clear at present.

The differences of Pt/PS, Pt/MgO and Pt/Al₂O₃ in catalytic properties were attributed to the different characteristics of the various supports. All the supported platinum nanocluster catalysts can be recovered by filtration and rinsing. The recovered catalysts exhibited the same activity and selectivity as before.

To get COL by selective hydrogenation of CAL, platinum catalysts have to be modified by such additives as iron, tin, germanium and cadmium [34–36]. Arai et al. [37] have improved the activity and selectivity of selective hydrogenation of CAL to COL using Al₂O₃-supported Pt catalyst prepared by NaBH₄ reduction at room temperature: selectivity to COL was 91% at 50% conversion of CAL, the average rate was 11.7 mol CAL (mol Pt h)⁻¹. However, when catalysed by Pt/PS, the selectivity for COL reached 94.7% at 79.7% conversion of CAL, and the average rate was 233.3 mol CAL

(mol Pt h)⁻¹. This result made an important step towards the goal of the research proposed by Boudart [38]: to be highly selective in the production of α,β -unsaturated alcohols from α,β -unsaturated aldehydes in nanocluster catalysis.

Note that the supported platinum nanoclusters also exhibited superior catalytic performances to Pt–PVP in other reaction systems. In the case of selective hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline, Pt/PS displayed higher activity and selectivity than Pt–PVP: the initial rates were 3.38 and 1.90 mol H₂ (mol Pt s)⁻¹ with 81.9% and 60.2% selectivity (at 100% conversion), respectively.

4. Conclusion

It has been pointed out that supports can strongly interact with tiny metal particles [19,38]. In the light of this view, Pt/PS has not yet revealed the entire potentiality of the platinum nanoclusters. Maybe a much better procedure will be found to display the full potentiality of the platinum nanoclusters in the near future.

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