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Preparation and immobilization of polymer-protected bimetallic colloids

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SUMMARY

Co–reduction of mixed metal ions of platinum–rhodium or rhodium–gold by refluxing its alcoholic solution in presence of a protective polymer results in a corresponding stable bimetallic sol, which in turn interacts with a suspension of silica gel, bearing thioether ligand, to give supported bimetallic catalysts. The TEM and XRD measurements indicate the formation of the bimetallic alloy clusters. The sols are used as catalysts for the selective partial hydrogenation of cis, cis–1.5–cyclooctadiene to cyclooctene. The bimetallic sol catalyst PVP–Pt–Rh shows an activity which is about twice as that of the monometallic sol PVP–Rh.

INTRODUCTION

Polymer–protected colloidal metal sols have attracted much attention in recent years. These metal colloids have successfully worked as catalysts for a variety of catalytic reactions such as hydrogenation[1], hydration of acrylonitrile[2], and photochemical evolution of hydrogen[3]. On the other hand, bimetallic catalysts have become the subject of increasingly intensive efforts both in industry and academia[4]. Because of numerous combinations possible, bimetallic catalysts have great potential to be tailored with respect to activity, selectivity and stability which can not be achieved by a single metal catalyst. Of supported bimetallic or multi–metallic catalyst, the activities and selectivities are greatly influenced by the electronic and conformational properties of its components as well as its composition and the geometric factors involved at the metal surface. In an ordinary route for preparation of bimetallic catalyst a suitable carrier such as silica is co–impregnated or successively impregnated with an aqueous solution of salts of the two metals of interest. The material is then dried and the metal precursors are reduced to the metallic state with a stream of hydrogen. In this communication, a procedure of preparation of polymer–protected bimetallic colloids is introduced. A stable platinum–rhodium or rhodium–gold bimetallic sol with a narrow particle size distribution was obtained by refluxing alcoholic solutions of mixed metal ions of interest in the presence of a protective polymer[5]. Using a method so–called as coordination capture which was recently proposed by us[6], immobilization of bimetallic sols on a carrier can be achieved via coordination with anchored ligands, providing a variant on supported bimetallic catalyst preparation. The only prerequisite for the bimetallic sol preparation is that the metallic component ions are similar in its reducibility. This alternative approach to preparation of the supported bimetallic catalyst could bring us several potential advantages: (1) Bimetallic particle size distribution usually can be controlled within a narrower range by the formation of colloidal sols; (2) The presence of the anchored ligands will exert an additional effect on the catalytic properties of the catalyst.

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EXPERIMENTAL

Materials and Equipment

Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), chloroauric acid ($HAuCl_4 \cdot 4H_2O$) are analytical reagent grades supplied by Beijing Chemicals Co. Rhodium trichloride hydrate ($RhCl_3 \cdot 3H_2O$) was prepared according to the literature method[7]. Poly (N–vinyl–2–pyrrolidone) was purchased from BASF. Methanol, extra pure grade, from Beijing Chemicals Co. was used without further treatment. Cis, cis–1.5–cyclooctadiene > 98%(GC) from Fluka was purified by the standard procedure prior to use. Anchored thioether ligands on silica were prepared by treatment of a suspension of silica in toluene with EtS $(CH_2)_3$–$Si(OMe)_3$ under reflux as described in the literature[8]. TEM examination was carried out using a Hitachi H–800 microscopy. Specimens were prepared by allowing a drop of the sol supported over a copper grid covered with a perforated carbon film. XPS data were obtained with a Kratos AEI ES–300 spectrometer. X–ray powder diffraction measurements were made with a Rigaku D/Max–3B diffractometer employing CuKα radiation. Specimens were prepared simply by evaporation of metallic sols, the physical mixture of PVP–Pt and PVP–Rh was made by mixing the PVP–Pt sol and PVP–Rh sol in 1:1 molar ratio then evaporated to dryness.

Preparation of Bimetallic Sols

A poly (N–vinyl–2–pyrrolidone) (PVP) – protected platinum–rhodium bimetallic sol was prepared similar to a reported method for monometallic sol[1]: $H_2PtCl_6 \cdot 6H_2O$ (10mg, 0.019 mg atom Pt). $RhCl_3 \cdot 3H_2O$ (4.2 mg, 0.016mg atom Rh) (Pt: Rh= 1.19 molar ratio), and PVP (150mg, 1.34 mmol as monomeric unit) were dissolved in a methanol–water mixed solvent (1:1 by volume, 50ml) and then refluxed for 4h. A dark red Pt–Rh bimetallic sol (PVP–Pt–Rh) was obtained. PVP–protected Rh–Au bimetallic sol (PVP–Rh–Au) was prepared with base accordingly[1]. A silica gel bearing ethyl thioether ligand (Si–S–Et, 32 mg. S content: 2.6%, 0.026 mmol S) was suspended in a PVP–Pt–Rh (20 ml, 0.014 mg atom M, S:M = 1.86). The suspension was stirred at room temperature for 24 h. The completion of the immobilization was ascertained by thorough discolouring of the solution phase leaving a great portion of protective polymer in liquor as verified by elementary analysis.

Hydrogenation of Cyclooctadiene

Into a 30ml flat–bottom flask were pipetted 1 ml metallic sol catalyst, 18 ml methanol. Hydrogen was introduced to replace air for several times. The catalyst was activated under the atmosphere of hydrogen with magnetic stirring for 0.5 h at 30°C. Cis, cis–1.5–cyclooctadiene (0.5 mmol in 1 ml methanol) then was charged and the hydrogenation reaction rate was measured by the uptake of hydrogen.

RESULTS AND DISCUSSION

An X–ray photoelectrospectroscopy (XPS) study on polymer–protected metallic sols was carried out and the XPS data showed that rhodium, platinum and gold in the sols appeared to be in a zero oxidation state (Table 1). H_2PtCl_6 , $RhCl_3$ or $HAuCl_4$ was refluxed respectively in the presence of PVP in a methanol–water mixed system, Pt (IV) , Rh(III) and Au(III) were reduced to the metal state by the alcohol and formed metallic sols. While mixing H_2PtCl_6 and $RhCl_3$, or $RhCl_3$ and $HAuCl_4$ in a solution under the same condition, Pt (IV) and Rh(III) or Rh(III) and Au(III) were co–reduced by refluxing alcohol and a bimetallic sol resulted. If the two metal components of the mixed salts solution were greatly different in its reducibility, bimetallic sols could not be made by this manner[10].

TEM measurements illustrate that Pt–Rh alloy particles in PVP–Pt–Rh sol (Fig.1a) are mostly distrituted in the range of 2.8–4.0nm with an average diameter of 3.4 nm and that Pt particles in

PVP–Pt sol (Fig.1d) and Rh particles in PVP–Rh sol (Fig.1e) are in 1.2–2.0nm with an average diameter of 1.6nm or in 3.0–4.3nm with an average diameter of 3.5nm respectively. Furthermore, there are some aggregates consist of several particles to dozens of particles in PVP–Pt sol and in PVP–Rh sol, while are not in PVP–Pt–Rh bimetallic sol. The mechanisms of formation of well distributed bimetallic sols have yet to be studied.

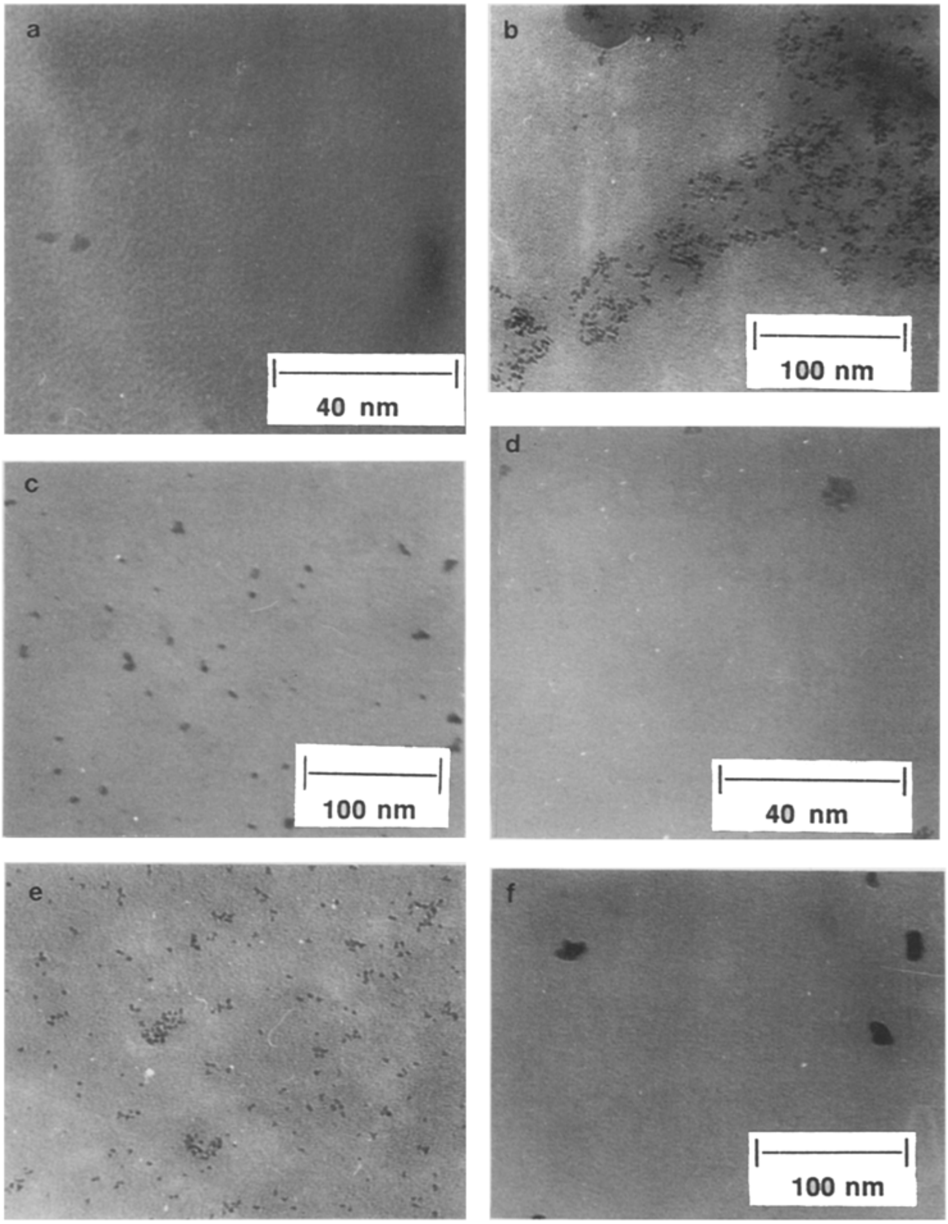


Figure1 TEM micrograph a . PVP–Pt–Rh, b. SiO_2-Immobilized PVP–Pt–Rh, c. PVP–Rh–Au, d. PVP–Pt, e. PVP–Rh, f. PVP–Au

Table 1. XPS Data for Polymer–Protected Metallic Sols and Related Substances

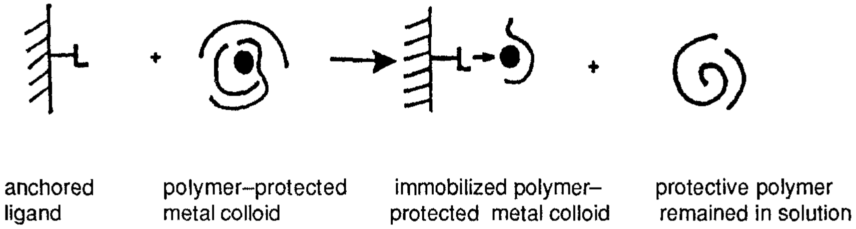
Compound	Bindinig Energy, [a] eV Rh $3d_{5/2}$	Pt $4f_{7/2}$	Au $4f_{7/2}$
PVP–Rh	307.0		
PVP–Pt		70.6	
PVP–Au			83.9
PVP–Pt–Rh	306.7	70.1	
PVP–Rh–Au	307.2		84.1
Rh (Metal)[b]	307.0		
Pt (Metal)[b]		70.6	
Au(Metal)[b]			83.8

a The binding energy values are referred to C_{1S} (285.0 eV)

b From Ref. 9.

It is worthwhile to note the X–ray diffraction results of the sols, although both Pt particles in PVP–Pt sol and Rh particles in PVP–Rh sol are in crystalline state, the crystallinity of Pt particles is higher than that of Rh particles. Talking about the colloidal metal catalysts, wide attention has been paid in literatures to the metal particle size and its distribution [11], on the other hand, the crystallinity of the metal was scarcely considered. However, the crystallinity of the particle is directly related to the sort and the amount of the structural defects, the defects on the surface are believed to contribute to the active species in the heterogeneous catalysis. The formation of PVP –Pt–Rh bimetallic alloy clusters phase is evident from the diffraction patterns , which exhibit diffraction lines at positions approximately midway between the positions of the corresponding lines for PVP–Pt and PVP–Rh sols (see Fig.2) . Fig.3a is a pattern for a physical mixture of PVP–Pt sol and PVP–Rh sol contained the same absolute amounts of Pt and Rh as the PVP–Pt–Rh bimetallic sol used in obtaining the pattern in Fig.2c. The diffraction pattern of the physical mixture of PVP–Pt and PVP–Rh sol (Fig. 3a) consists of overlapping lines for the two individual types of sols and is clearly different from that of the PVP–Pt–Rh bimetallic sols (Fig. 3b)

The immobilization process of colloidal particles by anchored ligands via coordination capture can be visualized as shown in scheme 1.



Scheme 1

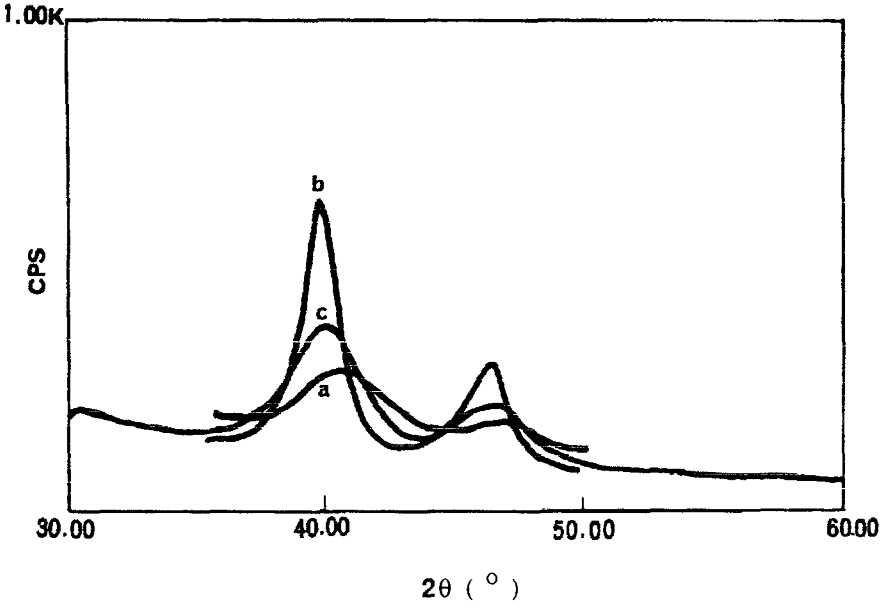


Figure 2 X-ray diffractograms for monometallic sols (a. PVP-Rh, b. PVP-Pt) and bimetallic sol (c. PVP-Pt-Rh)

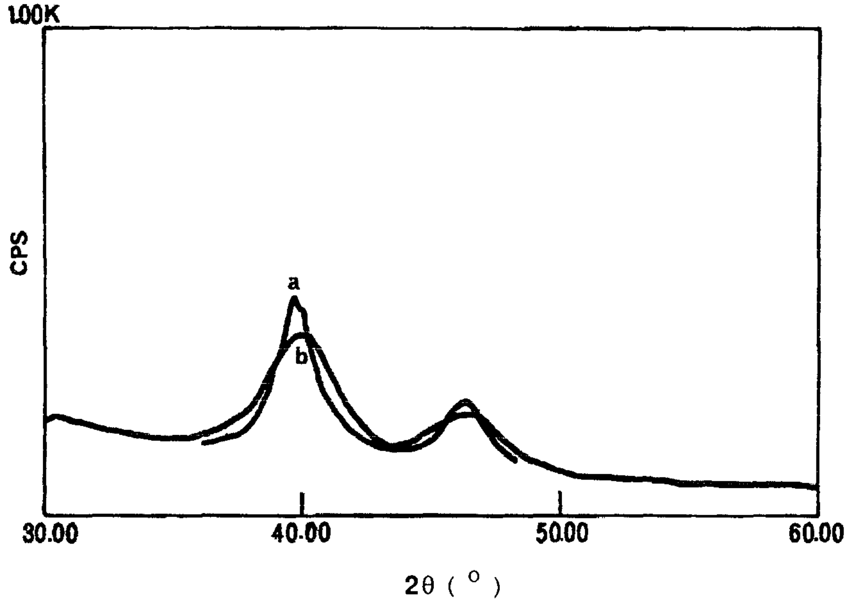


Figure 3 X-ray diffractograms for
a. the physical mixture of PVP-Pt and PVP-Rh, and b.bimetallic sol.

The efficiency of the coordination capture is expected to be determined by the difference in the coordination abilities between anchored ligand and protective polymer to the metal. The stronger the affinity of the anchored ligand to metal, the better the efficiency of the coordination capture is. The experimental results indicate that with Si–S–Et as ligand, PVP–Pt sol obtained from MeOH–H_2O is easily immobilized at a S:Pt ratio of 2:1 ; while for PVP–Rh sol, immobilization can merely complete in S:Rh > 8. This is because the anchored ligand Si-S–Et has a better affinity to Pt than Rh. The PVP–Pt–Rh/MeOH–H_2O can be thoroughly captured by Si–S–Et at S:M=1.8, which differs from PVP–Pt or PVP–Rh and implies that the sol is a bimetallic Pt–Rh sol other than a mixture of discrete Pt and Rh sols. No aggregation of metal particles occurs during the immobilization as verified by TEM (see Fig.1b) , and the XPS or XRD data also remain unchanged after immobilization.

For the hydrogenation of cis, cis–1.5–cyclooctadiene PVP–Pt sol is nearly inert. The initial rate of hydrogenation of cis,cis–1.5–cyclooctandiene is1.9 mol H_2 /g·atom Rh with PVP–Rh sol as catalyst, while under the same conditions, PVP–Pt–Rh sol catalyzes the hydrogenation at a initial rate of 3.8 mol H_2/g·atom Rh, which is about twice of that of the PVP–Rh sol. The reasons caused the higher activity for the PVP–Pt–Rh are probably due to the well dispersion of the bimetallic particles as verified by TEM observation, or due to the influence of platinum on the electronic or conformational properties of rhodium at the metal surface. Thus, these results do again demonstrate the formation of the bimetallic alloy clusters phase.

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REFERENCES

1. H. Hirai, Y. Nakao and N. Toshima, J. Macromol. Sci., Chem., A **13**, 727 (1979); H. Hirai, H Chawanya and N. Toshima, React. Polym.,**3**, 127 (1985).
2. H. Hirai, H. Wakabayashi and M. Komiyama, Chem. Lett., 1047(1983).
3. P. – A. Brugger, P. Cuendet and M. Gratzel, J. Am. Chem. Soc.,**103**, 2923 (1981).
4. J. H. Sinfelt, 'Bimetallic Catalysts', Wiley; New York, (1983); Acc. Chem. Res.,**10**, 15 (1977).
5. During our manuscript preparation, a closely related work was published by N. Toshima, K. Kushihashi, T. Yonezawa, and H. Hirai, Chem. Lett., 1769 (1989), in which a Pd–Pt bimetallic sol was prepared and characterized by TEM and spectrophotometric measurements.
6. Y. Wang, H. Liu and Y. Jiang, J. Chem. Soc., Chem. Commun., 1878(1989).
7. H. Liu, Huaxue Tongbao (Chemistry (China)) 531 (1981).
8. H. Liu and G. Mao, Fenzi Cuihua (J. Mol. Catal., (China)) **3**, 110 (1989).
9. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and B. E. Muilenberg (Ed.), 'Handbook of X–Ray Photoelectron Spectroscopy', Perkin–Elmer, Physical Electronics Division, Eden Prairie, 1979, p. 108, p. 152, p. 154.
10. V. M. Deshpande and C. S. Narasimhan, J. Mol. Catal.,**53**, L21 (1989).
11. H. Hirai and N. Toshima, in 'Tailored Metal Catalysts' ed. Y. Iwasawa, Reidel Publ. Co., Dordrecht pp. 121–135, (1986).

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