

Carbonylation of methanol catalyzed by polymer-protected rhodium colloid

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Abstract

Poly(*N*-vinyl-2-pyrrolidone)(PVP) protected rhodium colloid (Rh–PVP) was used as a catalyst for methanol carbonylation under elevated temperature (140°C) and high pressure (5.4 MPa). The activity of Rh–PVP colloid catalyst increased while recycled for 6 times totally lasting 56.5 h. During the reaction, the catalyst was still in a colloidal state verified by TEM observation. XPS and IR studies of the catalyst demonstrated that colloidal rhodium metal particles partially changed to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ under the reaction conditions. The rhodium ions in the reaction mixture amounted to 29% of the total charged rhodium after 13 h carbonylation. An additional XPS investigation of the catalyst was carried out; the results showed that oxidative addition of methyl iodide to rhodium colloid caused the transformation of rhodium species from Rh^0 to Rh^{1+} .

Keywords: Rhodium colloid; Carbonylation; Methanol; Polyvinylpyrrolidone

1. Introduction

Nanoscale metal colloids and clusters have aroused great interest among chemists and physicists because they offer unique surface chemical and physical characteristics [1]. In the field of chemistry, most studies on metal colloids have been concentrated on synthesis of different metal colloids with small size and narrow dispersion, as well as their application as catalysts [2,3]. Protected colloids have been used extensively for catalytic hydrogenation of various alkenes, alkynes or polyenes in liquid media [3–5]. More recently, photo-induced hy-

drogen generation [6], hydration of acrylonitrile [7], and hydrosilylation of alkenes [8] were catalyzed by platinum group monometallic or bimetallic colloids. However, these reactions were all carried out under rather mild conditions. It will be valuable to explore the possibility of conducting the reactions catalyzed by metal colloids under severe conditions. Methanol carbonylation of which reaction conditions are severe, is an important industrial process. After the technology of homogeneous rhodium catalyst system exploited by Monsanto Corporation was applied, extensive investigations about the rhodium catalyst system have been conducted on the mechanism, effect of promoters, solvents and additives in reaction media [9,10]. How-

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ever, using rhodium colloid as a catalyst in liquid phase carbonylation has not been involved, and the protective polymer PVP may have an improved effect on reaction rates, reported by patents [11], so it will be beneficial to utilize the Rh–PVP colloid as catalyst for more knowledge on carbonylation. In this paper, catalytic studies on the Rh–PVP colloid mediating carbonylation are reported.

2. Experimental

2.1. Materials and equipment

PVP (av. MW 10000, Aldrich), gelatine, methyl iodide, methanol were commercial products (analytical grade) and used without further purification. Rh–PVP colloid was prepared according to the literature [12]. By evaporating the solvents under reduced pressure via a rotating evaporator, the Rh–PVP colloid solid residue was redissolved in quantitative methanol to give a solution with a rhodium concentration of 7.2×10^{-3} M for reaction.

Gas chromatographic analysis was accomplished by temperature-programmed gas chromatographic technique using a Shanghai GC-8810 apparatus equipped with a 2 m PTFE column packed with GDX-203 stationary phase and with a thermo-conductivity cell detector.

TEM examination were operated on the equipment of Hitachi H-7000. Samples were prepared by placing a drop of the reaction solution, appropriately diluted, on a 3 mm copper grid which was covered with a perforated carbon film and placed on a disk of filter paper to remove excess solution. The TEM magnification on the sample was 12 000 or 15 000 and the TEM photograph was further magnified by 3 to 3.5 times for final measurement. The particle size distribution histogram was obtained on the base of about 300 particles per measurement.

IR spectra were recorded on a Bruker IFS-25 infrared analyzer with a resolution of 2 cm^{-1} . In a typical run for IR determination, the rhodium colloid (1.9×10^{-4} mol), methyl io-

dide (1 ml), and methanol (25 ml) were mixed and charged in a 150 ml autoclave with carbon monoxide (3.0 MPa at 27°C), then heated to 140°C to start the reaction. After a period of 1 h carbonylation, sample solution was squeezed out by the pressure in autoclave into a nitrogen permeated tube at ambient temperature. The solution in the tube was pumped into a 0.2 mm thick liquid cell with KRS-5 windows and transferred back into the tube. The absorption cell and the recycle line were filled with methanol to keep the circular system out of air prior to use. Methanol was selected as background for all samples.

2.2. XPS studies

Ordinary preparation of the specimen of a polymer-protected metallic colloid dispersion by evaporation was unsatisfactory for XPS determination owing to the coverage of protective polymer on the metal particle surface [4]. By the coordination capture technique indicated in literature [5], the rhodium in solution, both in ionic and colloidal states, can be transferred onto the surface of SiO_2 particle, which makes the XPS measurement possible. SiO_2 particle functionalized by thio-ether group and Rh–PVP solution with a molar ratio of S:Rh = 3.7:1 were mixed in a test tube and stirred under N_2 atmosphere at 30°C for 12 h. The solid was separated by centrifugation under the protection of N_2 , dried under vacuum, then measured on a PHI 5300 ESCA system (Perkin–Elmer) at once. Mg $\text{K}\alpha$ served as energy source and C 1s as internal standard.

Separation of rhodium ions from rhodium colloid was brought about by superfiltration. The superfiltration membrane used with an average hole diameter of 0.22 μm , which retarded the molecules with a molecular weight above 3000 was supplied by the Institute of Photographic Chemistry, the Chinese Academy of Sciences. The concentration of rhodium ions in the filtrate was determined by atomic absorption spectrometry (AAS).

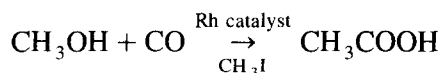
2.3. Carbonylation reaction

A typical procedure was as follows: Into a 150 ml autoclave the rhodium catalyst (3.8×10^{-5} mol), methyl iodide (4 ml), and methanol (20 ml) were pipetted. Nitrogen was introduced several times to replace air, and then carbon monoxide was charged to 3.0 MPa (at 27°C). The autoclave was heated to 140°C, when the reaction temperature was reached within ca. 50 min, the stirring was started and the pressure of the system was monitored. The reaction usually lasts for 10 h for each run. After a run, the reaction mixture which appeared clear and thoroughly homogeneous without any precipitate was analyzed by GC and then evaporated under reduced pressure to dryness. If needed, the solid residue was repeatedly redispersed in methanol as a reused catalyst for the successive run under the same condition.

When carbonylation was conducted under different temperatures, from ca. 130–160°C, the reaction time was controlled by stopping the carbonylation by rapid cooling the autoclave with an ice–salt mixture at about 10% conversion of methanol and thus the apparent activation energy was derived from the analytical data.

3. Results and discussion

The carbonylation reaction of methanol in this case was carried out as follows:



The activity of different catalysts were shown in Table 1. The data in Table 1 indicate that the Rh–PVP colloid was an active catalyst in the carbonylation of methanol, but its activity is lower than Monsanto's homogeneous catalyst. Another point is that addition of PVP or gelatine increase the activity of the homogeneous catalyst, which is consistent with the results of described in patents [11].

Table 1

The activities of different catalysts in carbonylation of methanol

Catalyst	Catalyst amount (g)	Rh amount (10^{-5} mol)	Activity (mol AcOH/mol Rh h)
RhCl ₃ ·3H ₂ O	0.0101	3.83	368
Rh–PVP colloid	0.1796	3.81	214
RhCl ₃ ·3H ₂ O + PVP	0.1826	3.87	421
RhCl ₃ ·3H ₂ O + gelatine	0.1787	3.68	452

Reaction conditions: Temperature = 140°C, Reaction time = 10 h, $P_{\text{CO}} = 3.0$ MPa, MeOH = 20 ml, MeI = 4 ml.

From literature [13], when the rhodium ions in Monsanto's homogeneous catalyst aggregated to clusters or metal precipitate during the carbonylation, the catalyst will lose its reactivity. The rhodium colloid with nanoscopic size, however, exhibits high activity in this reaction. This may be due to the high dispersion of colloidal catalyst in the reaction media. In order to study the stability of this catalyst, the Rh–PVP colloid was repeatedly used for six times. The average rates of the catalyst shown in Table 2 gradually increase upon repeated use. These results allude a transformation of the catalytic species. Thus, TEM, IR and XPS measurements were carried out.

The reaction mixture was thoroughly homogeneous and clear without any precipitate after each run, TEM observation of the reaction solution were taken to find out if there are any changes in particle shape and size or others. The transmission electron micrographs and the corresponding particle size distribution histograms of the rhodium colloid before and after carbonylation are shown in Fig. 1.

It is seen from the figure that the particle size of rhodium colloid grew up in the course of

Table 2

The stability of colloidal Rh catalyst in carbonylation of methanol

Catalyst	Activity (mol AcOH/mol Rh h)					
	1st batch	2nd batch	3rd batch	4th batch	5th batch	6th batch
Rh–PVP	214	338	388	359	396	416

Reaction conditions: The same as in Table 1.

reaction. The initial average diameter of colloidal particles was 2.24 nm ($\sigma = 0.6$ nm) prior to use, after 2.5 h and 56.5 h carbonylation the diameters of particles became 3.5 nm ($\sigma = 0.7$ nm) and 5.7 nm ($\sigma = 1.7$ nm), respectively. For all the results of TEM observation have elucidated that the rhodium particles are in a colloidal state during the carbonylation. However, it is obviously unreasonable to assume that the reaction is catalyzed by the colloidal particles

themselves (by way of heterogeneous catalysis) with increasing in activity for 1.9 times while decreasing in surface area of particles for 2.4 times.

Carbon monoxide is a reactant in the carbonylation, furthermore, CO adsorbed or coordinated on different rhodium species exhibits its characteristic IR spectrum. Fig. 2 is the IR spectra showing the carbonyl stretching modes of different rhodium catalysts in various treat-

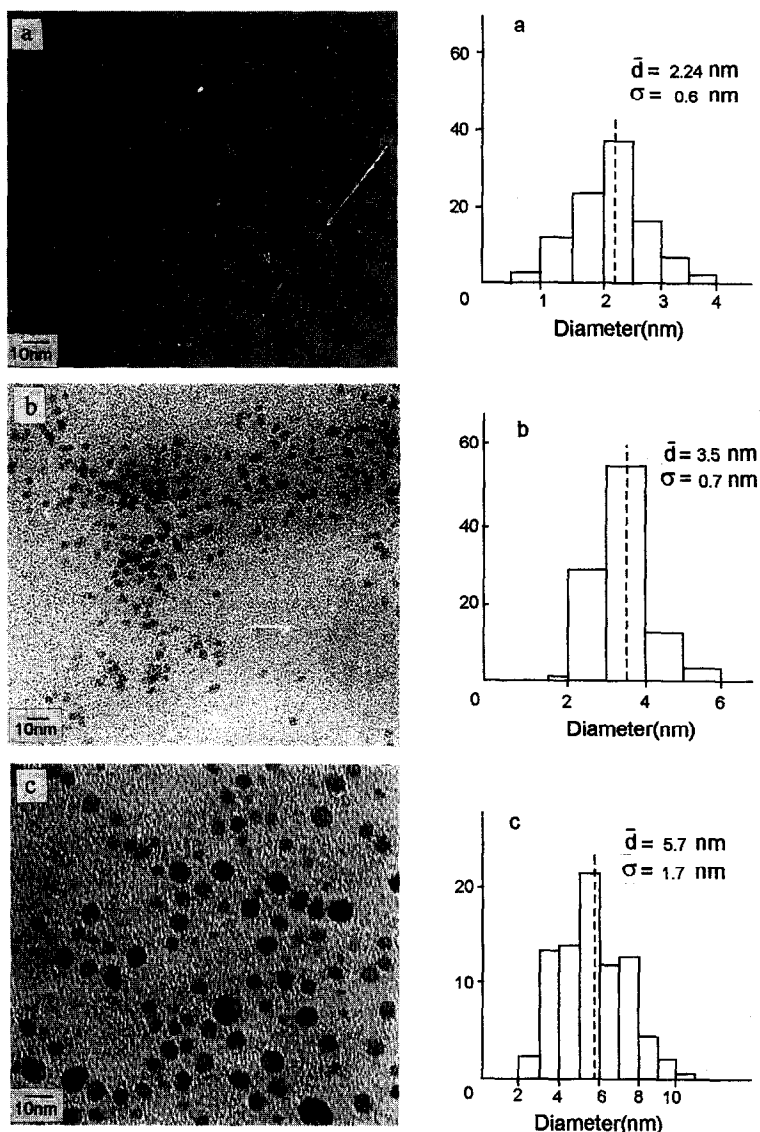


Fig. 1. The transmission electron micrographs and the particle size distributions of different Rh-PVP solution. (a) Rh-PVP colloid before reaction. (b) Reaction solution catalyzed by Rh-PVP colloid for 2.5 h. (c) Reaction solution catalyzed by Rh-PVP for 56.5 h.

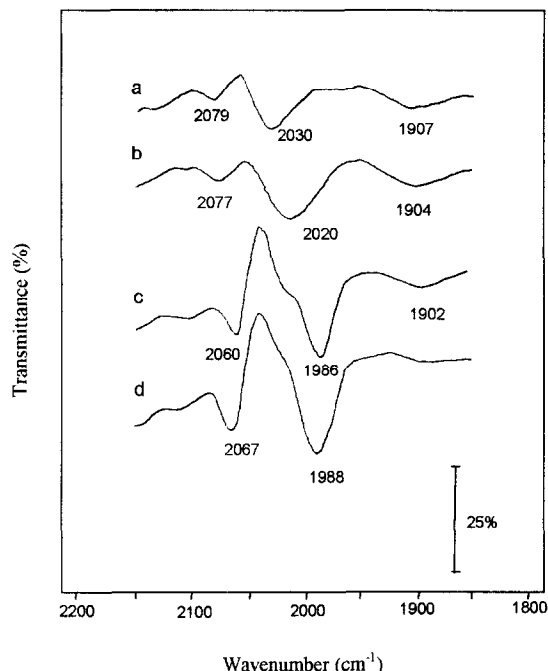


Fig. 2. IR spectra of (a) rhodium colloid sample after activation under 2.0 MPa H_2 at 60°C for 1 h, then saturated with 3.0 MPa CO at 60°C for 2 h; (b) rhodium colloid sample activated under 1.0 MPa H_2 for 2.0 h, then bubbled in CO for 40 min; (c) rhodium colloid sample after 1 h carbonylation reaction; (d) the reaction solution catalyzed by $RhCl_3 \cdot H_2O$ for 0.5 h.

ments. A Rh–PVP colloid sample in methanol was activated under 2.0 MPa H_2 at 60°C for 1 h, saturated with 3.0 MPa CO at 60°C for 2 h, then its IR measurement was taken. The spectrum shown in Fig. 2b has three CO absorption bands: 2077, 2020, 1904 cm^{-1} . Concerning the results reported by Mucalo et al. [14] of the CO adsorption on the Rh–PVA hydrosol, 2020 cm^{-1} band can be designated as linear stretching mode of RhCO, and 1904 cm^{-1} band as bridging stretching mode of Rh–CO–Rh, 2077 cm^{-1} band was attributed to the CO adsorption — two CO molecules per site [15,16]. In order to study the effect of CO pressure, the same Rh–PVP sample was then reactivated under 1.0 MPa H_2 at room temperature for 2 h, a stream of CO bubbled through the solution for 40 min, the IR spectrum of this solution shown in Fig. 2a declares that the 2079 cm^{-1} band which may be due to the asymmetrical vibration of two CO's per site still exist, but the band of linear

vibration mode shifts to higher frequency 2030 cm^{-1} . Moreover, the intensity of all CO absorption bands under atmospheric CO is weaker than those of at higher CO pressure, these suggested that more CO can interact with rhodium and the interaction is stronger under high pressure. Fig. 2d is the IR spectrum of the reaction solution catalyzed by $RhCl_3 \cdot 3H_2O + PVP$ for 0.5 h, the color of the solution is yellow, the two CO absorption bands at 2067 and 1988 cm^{-1} which intensity is about the same are the characteristic CO absorption band of $[RhI_2(CO)_2]^-$ by literature [10]. Fig. 2c shows the IR spectrum of a rhodium colloid sample Rh–PVP after 1 h carbonylation (The color of the solution is black.), two strong bands at 2060 and 1986 cm^{-1} with a small bulge at around 1902 cm^{-1} can be seen from the figure. This profile suggests a mixture of $[RhI_2(CO)_2]^-$ and a coordination patterns of CO on rhodium sol. It implies that a significant part of rhodium metallic colloid has changed into Rh^+ ion state under the reaction condition.

XPS determination was conducted by the method as described in the Experimental section. The binding energy of the component element ($Rh\ 3d_{5/2} = 307.4\ eV$) of the colloidal catalyst indicates that rhodium is in the metallic state [17] before reaction. After 9.5 h reaction, however, the rhodium in reaction mixture does not show a single peak, otherwise two binding energy peaks of $Rh\ 3d_{5/2}$ centered at 308.6 and 307.0 eV are observed according to the curve fitting. Compared with the literature values [17,18], they are attributed to Rh^{3+} and Rh^0 , respectively. This observation confirms that a part of rhodium colloid transformed into an ionic state which is in accordance with the IR results mentioned, firstly probably change to Rh^+ ions, and then oxidized to Rh^{3+} by HI (formed in carbonylation reaction) in the absence of CO during the XPS sample preparation [13].

The amount of rhodium ions generated after 13 h reaction at 140°C was determined by superfiltration and AAS analysis. The result shows

that about 29% colloidal rhodium changed into ions. According to the average rate of the $\text{RhCl}_3 \cdot 3\text{H}_2\text{O} + \text{PVP}$ catalyst, not strictly speaking, the 29% rhodium ions might contribute 57% of the total reactivity of Rh–PVP catalyst, and the 71% residual rhodium colloid contributed about 43%.

The CO IR spectrum gives us some information on the rhodium transformation, but CO is a reductive gas which can not oxidize the Rh^0 species. Comparing Fig. 2b and c, it can be seen that only CO can not make the substantial changes on Rh–PVP colloid catalyst. In order to clarify the transformation of Rh^{1+} to Rh^0 , a series of substrate combination experiments were performed. The oxidation state of rhodium species in solution under these experimental conditions were determined by XPS. The results are summarized in Table 3.

From experiment 1 and also the XPS data of the Rh–PVP colloid, it is clear that all the surface rhodium atoms are in the metallic state before reaction. Comparing the data listed in Table 3, we found that it is methyl iodide, not carbon monoxide, which most probably plays the predominant role in transferring rhodium species from Rh^0 to Rh^{1+} . This is consistent with the fact that the oxidative addition of organohalide to platinum metals can easily take place [19].

Table 3
Action of substrates on transformation of rhodium species^a

Entry	Rh (10^{-5} mol)	MeOH (ml)	AcOH (ml)	MeI (ml)	CO (MPa, at 27°C)	Rhodium species detected ^b
1 ^c	3.7	24	0	0	0	Rh^0 (307.4)
2 ^d	3.7	24	0	0	3.0	Rh^0 (307.4)
3	3.7	22	2.4	0	0	Rh^0 (307.3)
4	3.8	20	0	4	0	Rh^{1+} (308.0)
5	3.7	22.2	2.6	4	0	Rh^{1+} (307.8)

^a Experimental conditions: Temperature = 140°C, time = 9.5 h, P_{N_2} = 1.75 MPa.

^b Rhodium species were detected by XPS measurement, the binding energy of Rh $3d_{5/2}$ in eV for corresponding species are given in parentheses.

^c Colloidal rhodium sample prior to the carbonylation.

^d Carbon monoxide was used instead of nitrogen.

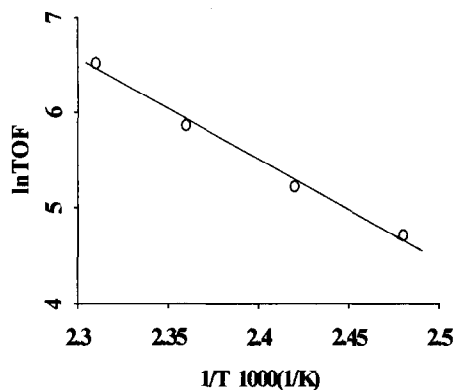
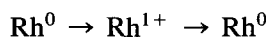


Fig. 3. The Arrhenius plot of Rh–PVP catalyzed carbonylation.

It can be drawn from the results of TEM, IR and XPS that during the reaction there is not only a dissolution of the rhodium particles but also a growing of the remaining particles, due to a subsequent reduction of rhodium (1) as the following sequence:



According to the literature [13], when the reaction medium is neutral or basic, CO will reduce the rhodium ions to clusters or metal propitiate. The increase of rhodium particle size may be explained as that when the rhodium catalyst was separated from the reaction products by evaporation and redispersed in methanol for the next run, at the beginning of reaction, the CO reduced Rh^{3+} on some colloidal rhodium particles in a neutral medium. The increase of rhodium particle size and the subsequent decomposition to rhodium ions are two competitive reactions. While recycling, some of the colloidal particles increased their size but were still kept in colloidal state, more rhodium changed to ions to make the rate increase gradually.

In addition, the activation energy of the reaction catalyzed by the Rh–PVP colloid was determined. The results were shown in an Arrhenius plot in Fig. 3. The apparent activation energy derived from the plot is 68.6 kJ/mol which is close to that of the homogeneous catalyst (61.5 kJ/mol reported by Hjortkjaer and Jensen [20]).

4. Conclusion

(1) The neat colloid Rh–PVP can be used as a catalyst for carbonylation under drastic conditions. The colloid metal catalyst kept in colloidal state for repeated use for 6 times lasting 56.5 h, the total turn-over-number reaches to 19 700 cycles/atom Rh.

(2) The Rh–PVP colloid partially changed into rhodium ions during carbonylation which could also be reduced on the colloidal rhodium surface to increase the colloid particle size.

(3) The oxidative addition of methyl iodide to the rhodium colloid probably accounts for the oxidation state change of rhodium species during carbonylation.

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