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Radiolytic preparation and catalytic properties of platinum nanoparticles

A.D. Belapurkar, S. Kapoor, S.K. Kulshreshtha, J.P. Mittal*

Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract

Stable Pt sols were prepared by the radiolytic reduction of H_2PtCl_4 in presence of protective water soluble polymer gelatin. The particle size and morphology were determined by TEM and found to be in the nm range. The catalytic activity of the sols was tested by hydrogenation of C_2H_4 at room temperature and compared with the standard Pt/Al_2O_3 catalyst. The effects of CH_3OH addition and glass support on the rate of the catalytic reaction were also investigated. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Study of nanosized metal particles is of great interest because of their potential applications in optical, electronic and magnetic devices [1–4]. Finely dispersed metal particles have found wide applications as catalyst materials. For heterogeneous catalysis, involving gas phase reactions, the noble metal particles are finely dispersed on the surface of inert oxide materials like Al_2O_3, SiO_2, TiO_2 etc [5]. Such catalyst are produced by impregnation of oxide powder with metal salt solution and its subsequent reduction in hydrogen stream leading to the formation of finely dispersed metal particles. For homogeneous catalysis where the reactants and products are in liquid phase, the metal particles need to be finely dispersed in the liquid phase in the form of stable sol. A variety of reducing agents have been

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* Corresponding author. Fax: +91-22-5505151.
E-mail address: mittaljp@magnum.barc.ernet.in (J.P. Mittal).

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used for the reduction of metals ions and the agglomeration of metal particles is prevented by using suitable capping reagent like PVA, PVP, gelatin and other polymers [6–8]. One of the major limitation of this method is the presence of excess reducing agent and the by products, produced during reduction process, which can affect the catalytic reactions. As most of the organic reactions are carried out in organic solvents, efforts have been made to produce finely dispersed metal particles in sol form by using alcohol reduction [9–11] Radiolytic reduction of metal ions in aqueous phase is a clean process [12–16]. The hydrated electron produced during the radiolysis of water is used for the reduction of metal ions. Here also the agglomeration of metal particles is prevented by suitable capping reagents. The shape and size of metal particles can be controlled by the relative concentration of metal ions and capping reagent [17,18].

There are very few studies dealing with the evaluation of the catalytic activity of radiolytically produced metal sols [19–22]. In the present communication, we report the preparation of Pt sol in water using radiolytic methods and evaluate their catalytic activity for a model reaction namely ethylene hydrogenation and results are compared with those obtained for the standard Pt/Al_2O_3 catalyst. The effect of adding methanol on the catalytic activity of Pt sol was also studied.

2. Experimental

Tetrachloroplatinic acid (Sigma) and gelatin (BDH) were used as received. All other chemicals were of HPLC, AR or GR grade. IOLAR grade N_2 gas (purity $>$99.9%) was used for purging the solutions. All solutions were prepared in Nanopure water (conductivity 0.06 $\mu S\ cm^{-1}$) just before the experiments and kept in dark to avoid photochemical reactions. Gelatin was allowed to swell in water for 15 minutes at ambient temperature and subsequently warmed at ~40–50°C for 2–3 min on water bath with continuos stirring so as to get a clear solution. Millimolar solution of chloroplatinic acid was prepared and added to the gelatin solution along with 0.1 mol dm^{-3} methanol as the OH radical scavenger. The mixed solution was purged with N_2 prior to gamma irradiation using ^{60}Co source with a dose rate of 20 Gy/min.

The formation of colloidal Pt nanoparticle was characterized by means of UV-vis spectrophotometry and transmission electron microscopy (TEM) (JEOL, JEM - 2000FX model). Samples for TEM studies were prepared by putting a drop of Pt sol on a copper grid coated with a thin amorphous carbon film. Samples were vacuum dried before putting them in TEM specimen holder.

γ-Al_2O_3 of 60–80 mesh size was impregnated with aqueous H_2PtCl_6 solution and reduced in 50% H_2-Ar gas mixture at 300°C. Reduced catalyst was cooled in H_2-Ar mixture to room temperature and flushed with Ar for ~1 hr. Catalyst so obtained contained 6.2 wt% Pt.

The catalytic activity of radiolytically prepared Pt sol for ethylene hydrogenation was studied in a closed glass reactor of 250 ml capacity at room temperature. The reactor was evacuated and filled with high purity argon at atmospheric pressure. 8 ml aqueous Pt sol containing different amount of Pt was injected in the reactor followed by injection of 10 ml C_2H_4 (3.33% v/v) and 40 ml H_2 (13.3% v/v). The reaction rate was monitored by analyzing gas mixture present in the reactor by gas chromatographic method (Chemito 850 model) using 8 feet porapak Q-S column and FID detector. Catalytic activity of Pt/Al_2O_3 with and without moisture was also evaluated using the same glass reactor.

Different amounts of methanol were added to aqueous Pt sol containing 40 mM Pt to study its effect on C_2H_4 hydrogenation under static conditions at room temperature. In these experiments same volume of methanol containing Pt sol having varying amounts of Pt, was used. For comparison activity evaluation was also carried out using Pt sol diluted with equal amount of water to account for the decrease in Pt concentration by methanol addition. Effect of various reaction parameters such as Pt metal concentration and the relative ratio of water and methanol present in Pt sol, was investigated with a view to see their effect on the reaction rate and product yield.

3. Results and discussion

Fig. 1a shows the absorption spectrum of Pt sol which is consistent with the results available in the literature [21]. Fig. 1b shows the TEM picture of these particles. The average size of platinum particles is found to be in the range of 10–20 nm.

3.1. Effect of Pt concentration on catalytic activity. Fig. 2 shows the plot of C_2H_6 formation as a function of time for two sols containing different concentrations of Pt along with the results of control experiments having no Pt particles. No ethane formation was observed in the absence of Pt. The amount of C_2H_6 formed increases monotonically with increase in reaction time and Pt concentration in aqueous sol. Based on the analysis of gas samples collected from the reactor at different time intervals, it was observed that ethane is the only reaction product as the total concentration of ethane and ethylene was found to be constant for all these samples.

3.2. Effect of methanol addition on catalytic activity. To study the effect of adding methanol on catalytic activity, the particles are produced in water because the radiolytic yield of solvated electron is more in water compared to methanol [23]. Ethylene hydrogenation reaction was studied in presence of various amounts of methanol (up to 25%) in aqueous Pt sol and the results are listed in Table 1. From this table it is observed that the catalytic activity of Pt particles is not affected by addition of large amount of methanol.

3.3. Effect of ageing. To test the stability of Pt nanoparticles the sol was kept under ambient conditions for three months. The extent of Pt precipitated was found to be almost negligible and the sol was found to be still active with almost same efficiency for C_2H_4 hydrogenation.

3.4. Glass supported Pt nanoparticles. Pt nanoparticles were found to strongly adhere on the surface of glass reactor. The Pt coating was found to be quite strong and could not be removed by washing with water and acetone. Pt coated reactor was evacuated after washing with water and acetone and used for C_2H_4 hydrogenation. The rate of C_2H_6 formation was found to be 2050 ml/hr.g Pt compared to 339 ml/hr.g of Pt observed over aqueous sol of Pt

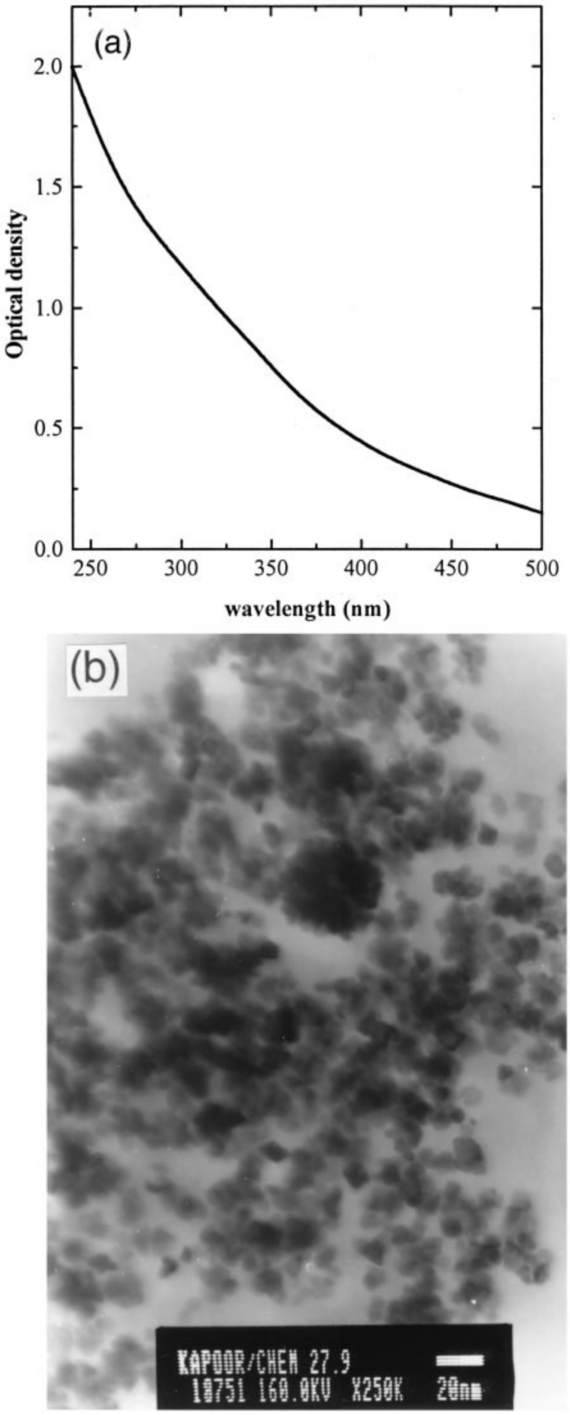

Fig. 1. (a) Absorption spectrum of Pt sol obtained on γ-irradiation of an N_2-bubbled solution containing 1.0×10^{-3} mol dm^{-3} K_2PtCl_4, 0.1% (wt/v) gelatin and 1.0×10^{-2} mol dm^{-3} methanol at pH 7. Dose = 480 Gy. (b) TEM picture for Pt particles.

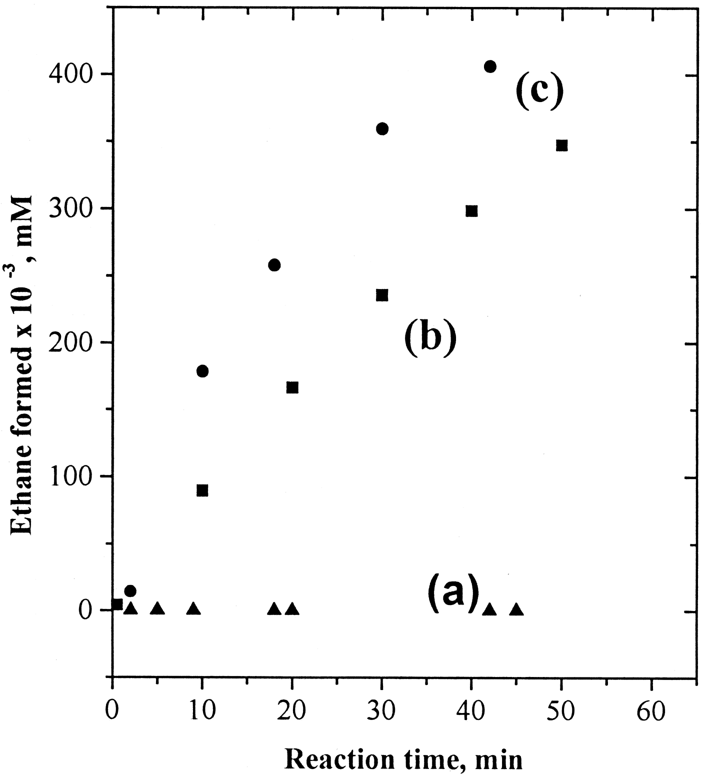

Fig. 2. Amount of ethane formed as a function of reaction time over Pt sol of different metal concentrations. (a) ▲ 0.0 M (b) ■ 25 mM (c) ● 40 mM.

nanoparticles. Lower activity of aqueous Pt sol may be due to lower mass transfer of the rectants C_2H_4 and H_2 to the surface of Pt nanoparticles which are surrounded by water molecules. No such constrain exists for glass supported catalyst. hence it shows higher activity.

3.5. Comparison of catalytic activity for Pt sol and Pt/Al_2O_3. Fig. 3(a) and (b) show the results of ethylene hydrogenation over the surface of dry Pt/Al_2O_3 and Pt sol, prepared by impregnation and radiolytic method respectively, for the same amount of Pt metal present in the sample. These results are almost comparable. However when 2 or 8 ml of water was

Table 1
Effect of methanol concentration in Pt sol on the rate of C_2H_6 formation

Serial No.	Methanol concentration in sol (mM)	Rate of C_2H_6 formation, ml/hr. g Pt
1	10	266.8
2	789	273.1
3	4930	250.0

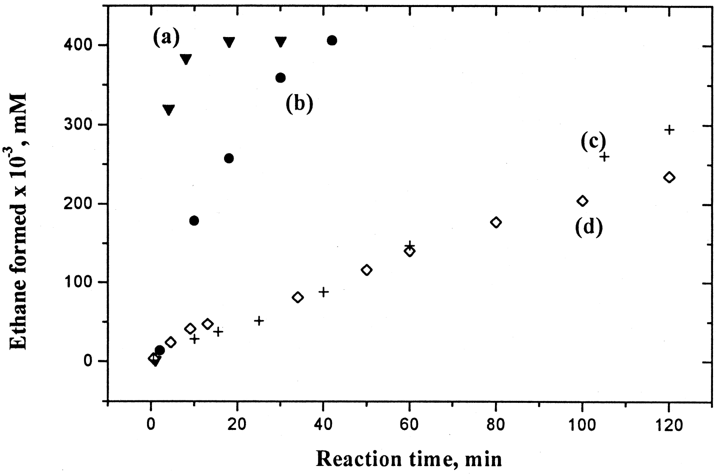

Fig. 3. Amount of ethane formed as a function of reaction time in samples containing 6.2 wt% Pt. (a) ▼ over dry Pt/Al_2O_3 (b) ● over Pt sol (c) + over Pt/Al_2O_3 immersed in 2 ml water (d) ◇ over Pt/Al_2O_3 immersed in 8 ml water.

added to Pt/Al_2O_3 catalyst the activity was found to be decreased significantly as can be seen from Fig. 3(c) and (d).

4. Conclusion

The above study shows that the aqueous sol of Pt prepared by radiolytic method shows good activity for C_2H_4 hydrogenation. The activity of Pt/Al_2O_3 in wet state was found to be significantly less than that of Pt sol. The hydrogenation activity of Pt sol is approximately proportional to its Pt concentration and the Pt nanoparticles supported on glass surface showed higher activity than aqueous Pt sol.

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