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# Catalytic oxidation of carbon monoxide over radiolytically prepared Pt nanoparticles supported on glass

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#### Abstract

Platinum nanoparticles have been prepared by radiolytic and chemical methods in the presence of stabilizer gelatin and SiO<sub>2</sub> nanoparticles. The formation of Pt nanoparticles was confirmed using UV–vis absorption spectroscopy and transmission electron microscopy (TEM). The prepared particles were coated on the inner walls of the tubular pyrex reactor and tested for their catalytic activity for oxidation of CO. It was observed that Pt nanoparticles prepared in the presence of a stabilizer (gelatin) showed a higher tendency to adhere to the inner walls of the pyrex reactor as compared to that prepared in the presence of silica nanoparticles. The catalyst was found to be active at  $\geq 150$  °C giving CO<sub>2</sub>. Chemically reduced Pt nanoparticles stabilized on silica nanoparticles gave ~7% CO conversion per hour. However, radiolytically prepared Pt nanoparticles stabilized by gelatin gave ~10% conversion per hour. Catalytic activity of radiolytically prepared platinum catalyst, coated on the inner walls of the reactor, was evaluated as a function of CO concentration and reaction temperature. The rate of reaction increased with increase in reaction temperature and the activation energy for the reaction was found to be ~108.8 kJ mol<sup>-1</sup>. The rate of CO<sub>2</sub> formation was almost constant (~1.5 × 10<sup>-4</sup> mol dm<sup>-3</sup> h<sup>-1</sup>) at constant O<sub>2</sub> concentration (6.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>) with increase in CO concentration from 2 × 10<sup>-4</sup> mol dm<sup>-3</sup> to 3.25 × 10<sup>-3</sup> mol dm<sup>-3</sup>. The data indicate that catalytic oxidation of CO takes place by Eley–Rideal mechanism. © 2005 Elsevier Ltd. All rights reserved.

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## 1. Introduction

In recent decades, there has been a considerable interest in the preparation and characterization of nanosized particles, both from fundamental and practical points of view [1-7]. The nanosize-associated catalytic activities have many potential applications. Worldwide attention has been aroused by the discovery of Haruta concerning the catalysis of Au nanoparticles [8]. In particular, the oxidation of CO has attracted a lot of interest because of its broad technological and fundamental importance [9-12]. The catalytic activity has been found to be sensitive to the size of the Au nanoparticles, the nature of the support and the method of preparation [13].

Central to the problem of oxidation of CO is the activation of oxygen molecules [14]. It is known that Au nanoparticles adsorb CO molecules well, they do not strongly adsorb and activate  $O_2$  molecules [15]. Thus, the oxide support often plays an important role in the activation of  $O_2$ . In this regard, large number of catalysts have been evaluated for oxidation reaction of CO [16–27]. Also, a lot of work has been carried out for the catalytic recombination of CO and  $O_2$  for application in sealed off CO<sub>2</sub> laser [28–31]. Various mechanisms have been proposed for explaining CO +  $O_2$  reaction [32–34]. In spite of these efforts, there is still scope for a better catalyst for application in sealed off CO<sub>2</sub> laser. For example, if an active, adherent, discontinuous film of small noble metal particles is coated inside a laser tube, it may be possible to recombine CO and  $O_2$  generated and maintain the optimum laser output.

In the present work, we report on the catalytic efficiency of radiolytically prepared Pt nanoparticles for  $CO-O_2$  recombination reaction. To mimic the conditions for practical applications, Pt nanoparticles were coated inside a tubular glass reactor and studied for  $CO-O_2$  recombination reaction under static reaction condition which is almost similar to one existing in  $CO_2$  laser tube. Also, an attempt was made to evaluate the catalytic efficiency of coated Pt nanoparticles with time to check the propensity for poisoning [35].

#### 2. Experimental

Tetrachloroplatinic acid (BDH), sodium borohydride (BDH), gelatin (BDH) and SiO<sub>2</sub> (Aldrich) were used as received. All other chemicals were of HPLC, AR or GR grade. Silica (SM-30, 30 wt.%) was obtained from Aldrich. IOLAR grade N<sub>2</sub> gas (purity > 99.9%) was used for purging the solutions. All the solutions were prepared in nanopure water (conductivity, 0.06  $\mu$ S cm<sup>-1</sup>) just before the experiments and kept in dark to avoid photochemical reactions. Gelatin was allowed to swell in water for 15 min at ambient temperature and subsequently warmed at ~40–50 °C for 2–3 min on a water bath with continuous stirring so as to get a clear solution. Millimolar solution of metal salts was prepared and added to the gelatin solution along with 0.1 mol dm<sup>-3</sup> methanol as °OH radical scavenger. The mixed solution was purged with N<sub>2</sub> prior to gamma irradiation using a <sup>60</sup>Co source with a dose rate of 20 Gy/min. The total dose used for irradiation was 1 kGy. Chemically reduced Pt nanoparticles were prepared by adding drop wise ice-cold sodium borohydride solution (10<sup>-3</sup> mol dm<sup>-3</sup>) to K<sub>2</sub>PtCl<sub>4</sub> solution (10<sup>-3</sup> mol dm<sup>-3</sup>) containing gelatin or SiO<sub>2</sub> nanoparticles (1.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>) which are used to prevent aggregation of Pt particles. These nanoparticles were then coated on the inner walls of the reactor and used for CO oxidation activity.

Colloidal metal particles were characterized by UV–vis absorption spectroscopy and transmission electron microscopy (TEM) [JEOL, JEM-2000 FX model]. Samples for TEM were prepared by putting a drop of the metal solution on a copper grid coated with a thin film of amorphous carbon. Samples were vacuum-dried before putting them in TEM specimen holder. A closed cylindrical glass reactor of 75 ml

capacity (24 cm length  $\times$  2 cm diameter) was etched with 10% HF solution, washed and dried. This dry reactor was soaked with the aqueous metal sol. The reactor was dried at 100  $^{\circ}$ C after draining all the sol. The procedure was repeated five times. Amount of Pt deposited was analysed by atomic absorption spectroscopy after dissolving in aqua regia and found to be 0.078 mg and 0.057 mg for radiolytically and chemically prepared Pt nanoparticles, respectively. Surface roughness of the metal coated reactor was evaluated using Mitutoyo Surftst-211 instrument. Catalytic activity of the glass-supported Pt nanoparticles was studied under static reaction condition using a metal-coated glass reactor. The reactor was evacuated and filled with high purity helium at atmospheric pressure. Different concentrations of  $CO [2 \times 10^{-4} \text{ mol dm}^{-3} \text{ to } 3.25 \times 10^{-3} \text{ mol dm}^{-3}]$  were used in the presence of fixed concentration of  $O_2$  $(6.5 \times 10^{-3} \text{ mol dm}^{-3})$  during CO oxidation reaction. The progress of the reaction was monitored by periodic analysis of the reactor content by gas chromatography [Chemito-8510] using TCD and 8 ft spherocarb column maintained at 100  $^{\circ}$ C. The rate of the reaction was calculated on the basis of the time required for 10% CO conversion. The effect of reaction temperature was studied by maintaining the reactor at a desired temperature [100–350 °C]. For comparison, CO oxidation by Pt nanoparticles, prepared by chemical reduction method and stabilized by SiO<sub>2</sub> nanoparticles, was evaluated under identical conditions. Also, thermal oxidation of CO was studied using the same reactor without metal coating.

# 3. Results and discussion

UV-vis absorption spectra for Pt sol prepared by  $\gamma$ -irradiation or chemical reduction were consistent with the reported data [36,37]. Fig. 1 shows a representative TEM picture of gelatin-stabilized radiolytically prepared Pt nanoparticles used for catalytic reactions. It can be seen that the size of Pt particles was in the range of 10–20 nm.

## 3.1. Catalytic oxidation of CO by gelatin-stabilized radiolytically prepared Pt nanoparticles

No detectable thermal reaction between CO and  $O_2$  was observed up to 500 °C in the absence of metal nanoparticles. To examine the catalytic reactions, Pt nanoparticles were deposited on the reactor



Fig. 1. TEM picture for radiolytically prepared Pt nanoparticles.

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walls. Cente line average (CLA) surface roughness of the Pt nanoparticles coated reactor was found to be 0.41  $\mu$ m. Glass supported Pt catalyst was found to be active for oxidation of CO at  $\geq$ 150 °C. Fig. 2a shows the amount of CO<sub>2</sub> formed (normalized to per milligram of Pt) as a function of the reaction time at 175 °C. It can be seen that the amount of CO<sub>2</sub> formed varies linearly with the reaction time.

The rate of catalytic CO oxidation was also studied as a function of temperature. It was found that the rate of catalytic oxidation increased with increase in the reaction temperature. The plot of  $\ln k$  versus 1/T was found to be a straight line (Fig. 3). Activation energy of the reaction was calculated to be  $\sim 108.8 \text{ kJ mol}^{-1}$ .

Fig. 4 shows the effect of CO concentration on the rate of  $CO_2$  formation at constant  $O_2$  concentration. It can be seen from the figure that when CO concentration was increased from  $2 \times 10^{-4}$  mol dm<sup>-3</sup> to  $3.25 \times 10^{-3}$  mol dm<sup>-3</sup>, the rate of  $CO_2$  formation remained constant at  $1.5 \times 10^{-4}$  mol dm<sup>-3</sup> h<sup>-1</sup>. This indicates that reaction occurs via Eley–Rideal mechanism [38] between chemisorbed CO and gaseous/ physisorbed  $O_2$ . As the rate of  $CO_2$  formation is constant, percent conversion of CO increases with decrease in CO concentration (Table 1). It is important to mention here that CO oxidation activity of Pt catalyst exposed to ambient air at room temperature for 9 months was found to be the same indicating that the catalyst is stable under ambient conditions.

#### 3.2. Catalytic activity of chemically reduced Pt nanoparticles

For comparison, K<sub>2</sub>PtCl<sub>4</sub> was reduced with NaBH<sub>4</sub> with and without gelatin. However, Pt nanoparticles so generated were found to agglomerate with time giving large particles that settled down easily.



Fig. 2. Variation in the yield of CO<sub>2</sub> (normalized to 1 mg of Pt) as a function of reaction time for catalytic oxidation of CO at 175 °C, CO =  $1.63 \times 10^{-3}$  mol dm<sup>-3</sup> and O<sub>2</sub> =  $6.5 \times 10^{-3}$  mol dm<sup>-3</sup>: (a) gelatin-stabilized radiolytically prepared Pt nano-particles and (b) chemically reduced Pt nanoparticles stabilized by SiO<sub>2</sub> nanoparticles.



Fig. 3. Effect of temperature on the catalytic activity for the reaction of CO oxidation over Pt nanoparticles prepared radiolytically in the presence of gelatin.

Hence, these particles were not used for measurements of catalytic activity. Therefore,  $K_2PtCl_4$  was reduced by NaBH<sub>4</sub> in the presence of SiO<sub>2</sub> nanoparticles as a dispersing medium. Pt nanoparticles so generated did not agglomorate and remained in the sol form for more than 1 month. CO oxidation activity of Pt nanoparticles so prepared was evaluated under an identical condition. It can be seen from Fig. 2b that the yield of CO<sub>2</sub> formed (normalized to per milligram of Pt) is higher for radiolytically prepared Pt nanoparticles stabilized by gelatin as compared to that for the chemically reduced Pt nanoparticles, stabilized by SiO<sub>2</sub> nanoparticles. Gelatin-stabilized Pt nanoparticles were supported on borosilicate (pyrex reactor) while chemically reduced Pt nanoparticles were supported on silica which in turn were coated on the reactor wall. Catalyst-supports are known to affect the catalytic activity [13]. This may be the probable reason for higher catalytic activity of the radiolytically generated Pt nanoparticles.



Fig. 4. Variation in the rate of  $CO_2$  formation with the change in the concentration of CO.

S. no.	Catalyst	Reactant concentration $(10^{-3} \text{ mol dm}^{-3})$		Reaction temperature (°C)	$CO_2$ formed (10 <sup>-3</sup> mol dm <sup>-3</sup> h <sup>-1</sup> )	CO conversion $(\% h^{-1})$
		CO	O <sub>2</sub>	( )	uni n )	(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
1	Nil	3.25	6.5	500	0	0
2	Pt nanoparticle coated on glass surface	3.25	6.5	175	0.15	4.6
3	Pt nanoparticle coated on glass surface	1.63	6.5	175	0.16	10.2
4	Pt nanoparticle coated on glass surface	0.83	6.5	175	0.13	15.5
5	Pt nanoparticle coated on glass surface	0.41	6.5	175	0.13	30.5
6	Pt nanoparticle coated on glass surface	0.2	6.5	175	0.14	70.9

Table 1		
Effect of CO concentration on the rate	of CO <sub>2</sub> formation over gelatin-stabilized	radiolytically prepared Pt nanoparticles

## 4. Conclusions

Radiolytically prepared Pt nanoparticles on glass support are active for oxidation of CO at  $\geq 150$  °C. Catalytic activity was found to increase with increase in reaction temperature. It appears that the radiolytically prepared catalyst can be used for longer duration of time as its activity was found to be the same even after 9 months. Also, the coating of gelatin-stabilized Pt nanoparticles over glass is more effective as compared to chemically reduced Pt nanoparticles. The present work shows that very small quantity of Pt is effective for oxidation of CO.

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