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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_2 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_2. 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^{-1}. The rate of CO_2 formation was almost constant (~1.5×10^{-4} mol dm^{-3} h^{-1}) at constant O_2 concentration (6.5×10^{-3} mol dm^{-3}) with increase in CO concentration from 2×10^{-4} mol dm^{-3} to 3.25×10^{-3} mol dm^{-3}. The data indicate that catalytic oxidation of CO takes place by Eley–Rideal mechanism.

Keywords: A. Nanostructures; C. Electron microscopy

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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_2 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_2 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_2 (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_2 gas (purity $> 99.9\%$) was used for purging the solutions. All the 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 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^{-3} methanol as $^{\bullet}OH$ radical scavenger. The mixed solution was purged with N_2 prior to gamma irradiation using a ^{60}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^{-3} mol dm^{-3}) to K_2PtCl_4 solution (10^{-3} mol dm^{-3}) containing gelatin or SiO_2 nanoparticles (1.5×10^{-3} mol dm^{-3}) 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