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Catalytic Oxidation of Carbonmonoxide Using Platinum Nanoparticles Synthesized in Microemulsion

[1]O.P. Yadav, [2]Y.K. Yadav, [3]A.R. Das, [3]Tania Dey, [4]Shailja Kakkar and [4]M.L. Singla
[1]Department of Chemistry, CCS Haryana Agricultural University, Hisar-125004, India
[2]Department of Environmental Sciences and Engineering,
Guru Jambheshwar University of Science and Technology, Hisar-125001, India
[3]Polymer Science Unit, Indian Association for the Cultivation of Science,
Jadavpur, Kolkata-700 032, India
[4]Department of MRD, CSIO, Sector-30, Chandigarh, India

Abstract: Platinum nanoparticles prepared by the interaction of Chloroplatinic acid (H_2PtCl_6). H_2O and hydrazine hydrate ($N_2H_4.H_2O$) in water-in-oil microemulsion [Polyoxyethylene-4-dodecylether ($C_{12}E_4$) + Cyclohexane (C_6H_{12}) + Water (H_2O)] in the absence and presence of poly(N-vinylpyrrolidone) (PVP) and Polyethylene Glycol (PEG) have been characterized using X-Ray diffraction (XRD), electron diffraction and transmission Electron Microscopy (TEM) techniques. Platinum nanoparticles adsorbed on alumina converted CO to CO_2 at much lower temperature (245°C) compared to 325°C when pure alumina was used as catalyst. The catalytic activity of the synthesized nanoparticles in microemulsion containing PVP, examined in terms of CO to CO_2 conversion reaction as a function of temperature exhibit higher catalytic efficiency compared with those synthesized in the microemulsion without PVP and microemulsion-PEG systems.

Key words: Nanoparticles, microemulsion, platinum, electron diffraction catalytic activity

INTRODUCTION

In order to achieve Super Ultra Low Emission Vehicle (SULEV) standards, a combination of precise engine fuelling, efficient in-cylinder combustion and a highly efficient Three-Way Catalyst (TWC) in the vehicle exhaust system is required. This research is an *in vitro* study to develop an efficient catalyst system which may eliminate carboumonoxide, one of the serious gaseous pollutants in the automotive exhaust (other than hydrocarbons and oxides of nitrogen and sulphur), at ambient low temperature (Twigg, 2003a, b). The catalytic activity of metals is known to be a function of the size and shape of the catalyst particles, their methods of preparation and the specific nature of the support material used (Grunwaldt and Baiker, 1999; Yadav *et al*., 2003). The noble metal nanostructures on metal oxide supports manifest catalytic behaviour towards chemical processes such as partial oxidation of hydrocarbons, reduction of nitrogen oxides, catalytic oxidation at low temperature.

The oxidative conversion of carbon monoxide (CO) to carbondioxide (CO_2) at low temperature is an important reaction and consequently various approaches have been employed for carrying out the oxidation reaction including those utilizing noble metal nanoparticles (Lopez *et al*., 2004; Yadav *et al*., 2003). A few chemical methods have yielded noble metal nanomaterials using stabilizers of diverse structural characteristics (Pileni *et al*., 1998; Chen *et al*., 2000). There are

Corresponding Author: O.P. Yadav, Department of Chemistry, CCS Haryana Agricultural University, Hisar-125004, India

a number of reports of nanoparticle formation in microemulsion medium. The droplet size of microemulsion can be manipulated by carefully designing its composition and thus offers the scope of synthesizing reasonably monodisperse nanoparticles.

This communication deals with our studies on the preparation of platinum nanoparticles by reducing (H_2PtCl_6). H_2O with hydrazine hydrate ($N_2H_4.H_2O$) in water-in-oil microemulsion composed of Polyoxyethylene-4-dodecyl ether ($C_{12}E_4$), Cyclohexane (C_6H_{12}), Water (H_2O) and a polymer (PVP or PEG), characterization of the synthesized nanomaterial using XRD, electron diffraction and TEM techniques and monitoring the catalytic performance of the synthesized nanomaterial in terms of conversion reaction of CO to CO_2 as a function of temperature.

MATERIALS AND METHODS

Cyclohexane (C_6H_{12}) (Merck); Chloroplatinic acid [H_2PtCl_6].H_2O (Sigma); tetrahydrofuran (THF) (Merck); Polyoxyethylene-4-dodecyl ether ($C_{12}E_4$) (Sigma); hydrazine hydrate ($N_2H_4.H_2O$) (Qualigens); poly(N-vinylpyrrolidone) (PVP) (Aldrich) (MW 30,000); Polyethylene glycol (PEG) (Aldrich) (MW 10,000) and alumina (γ-Al_2O_3) (Puralox/Condea) were used as received. Double distilled water (Sp. Conductivity: 2×10^{-5} S cm^{-1}) was used in all the experiments.

Microemulsions were prepared by mixing a suitable qnantity of aqueous [H_2PtCl_6].H_2O solution with the organic phase containing the surfactant ($C_{12}E_4$) and cyclohexane (C_6H_{12}). The concentrations of [H_2PtCl_6].H_2O and the surfactant ($C_{12}E_4$) in the prepared microemulsion were 0.01 and 0.1 M, respectively. In a few microemulsion samples a polymer (PVP or PEG) (0.5% W/V) was also incorporated. Hydrazine hydrate ($N_2H_4.H_2O$) (0.05 M) was added slowly to the microemusion sample to reduce Pt^{+4} ions to platinum metal.

The metal particles produced in the microemulsion were released by adding THF and directly adsorbed on alumina. The Pt: Alumina (1:50) powder isolated by vacuum filtration was calcined at 550°C for 1 h. The obtained product was cooled and then stored in a moisture-free atmosphere.

For synthesizing nanoparticles of varying size the ratio of water to surfactant (W) in the microemulsion was maintained at 5, 10 and 15. X-ray diffraction (XRD) profiles of the nanomaterials were recorded on a Philips analytical diffractometer (PW 1710 BASED) equipped with PC-APO diffraction software. Radiation of 1.5406 A° wavelength was used. Transmission electron microscope (TEM) images of platinum nanoparticles-on-alumina samples were obtained by a JEOL 200CX instrument (accelerating voltage 100 KV, beam current 20 μA, magnification 100 K). In order to carry out the catalytic oxidation of CO to CO_2 we used a vertical quartz-tube reactor having a porous frit in the middle. The details of the apparatus have been described elsewhere (Yadav *et al*., 2003).

A flow of CO (1%), O_2 (5%) and Argon (94%) was charged at one end of the reactor tube preloaded with Platinum-on-Alumina (0.1 g) catalyst. A quadrupole mass spectrometer (Balzers Quadstar 421) was used for qnantitative estimation of gas composition at the reactor outlet. The conversion reaction of CO to CO_2 was monitored over the temperature range of 25-550°C.

RESULTS AND DISCUSSION

The TEM images of the prepared nanomaterial by varying the ratio of water to surfactant (W) in the microemulsion are shown Fig. 1a and b. Figure 1c and d depict the particle size distribution. It is observed from the TEM images and their histograms that the size of freshly prepared platinum nanoparticles corresponding to water to surfactant (W = 10) and dispersed in cyclohexane (sample 1a) is smaller than those adsorbed on Alumina preheated at 550°C (sample 1b). This may be attributed to partial agglomeration of the nanoparticles at the high temperature employed.

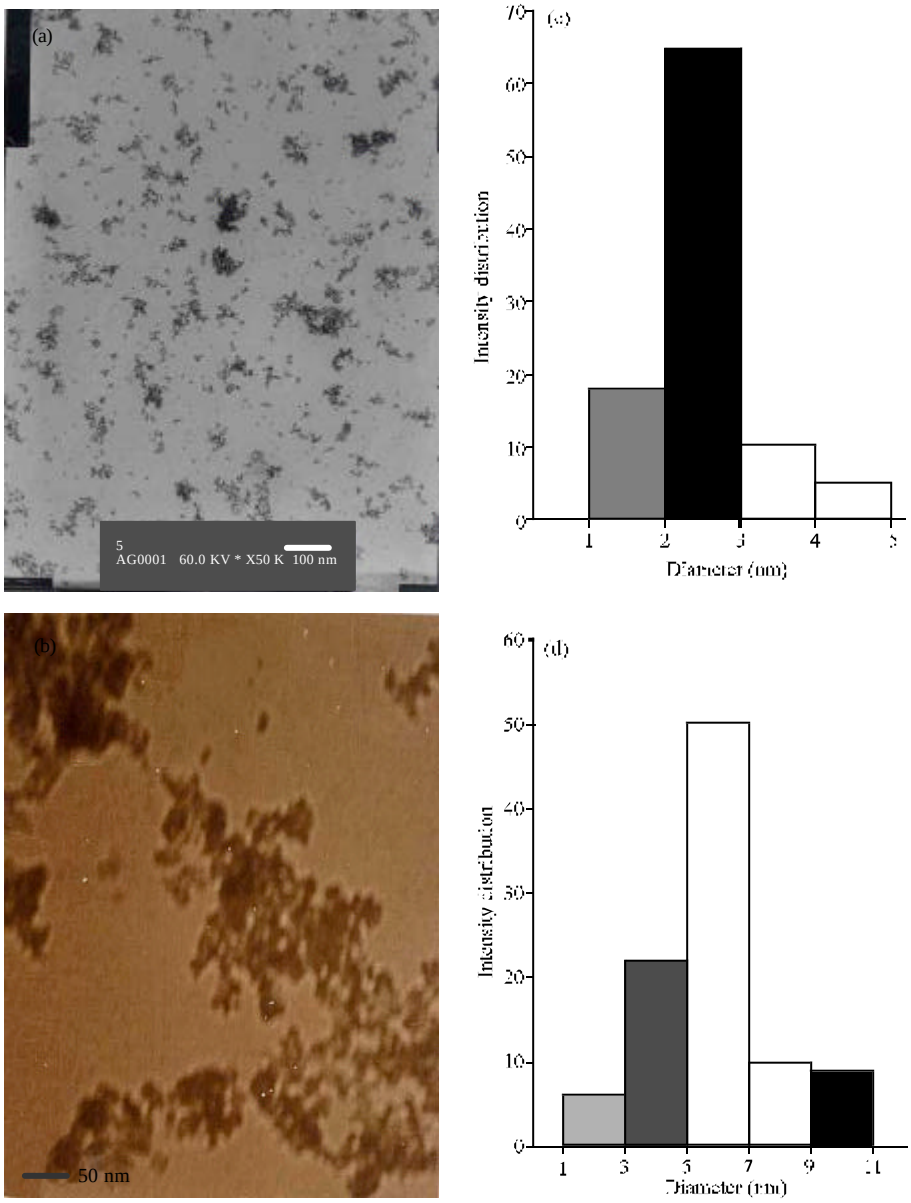

Fig. 1: Transmission Electron Micrograph (TEM) images of platinum nanoparticles synthesized in oil-in-water microemulsion ($C_{12}E_4$+water+C_6H_{12}): (a) freshly synthesized platinum nanoparticles dispersed in cyclohexane (W = 10) (b) platinum nanoparticles adsorbed on alumina and preheated at 550°C (W = 10). c and d correspond to TEMs a and b, respectively

The diffraction profiles depicts three reflections at 2θ = 36.7°, 39.5° and 46.3°. The reflection at 2θ = 39.5° and 46.3° are assigned to the (111) and (200) planes respectively of face centred cubic (fcc) crystal structure of platinum. However, the reflection at 2θ = 36.7° is assigned to (002) plane of the body centred tetragonal lattice suggesting the presence of mixed phase of the prepared platinum nanomaterials (Fig. 2). Electron diffraction image of platinum nanoparticles (adsorbed on alumina) prepared in microemulsion ($C_{12}E_4$+water+C_6H_{12}) (W = 10) (Fig. 3).

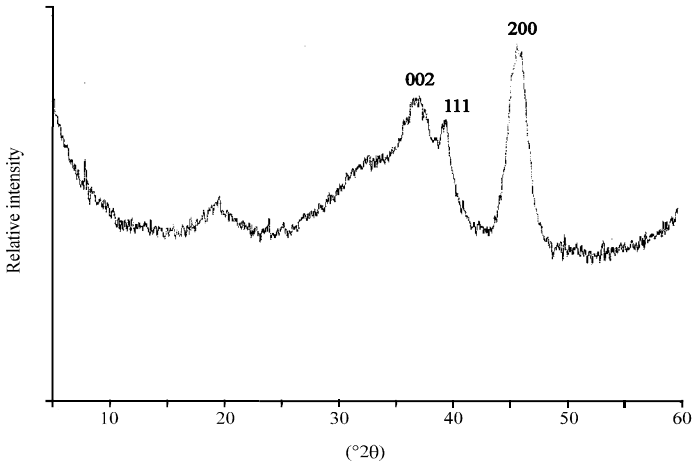

Fig. 2: The XRD spectra of platinum nanoparticles (adsorbed on alumina) synthesized in water/oil microemulsion ($C_{12}E_4$+water+C_6H_{12}) (W = 10)

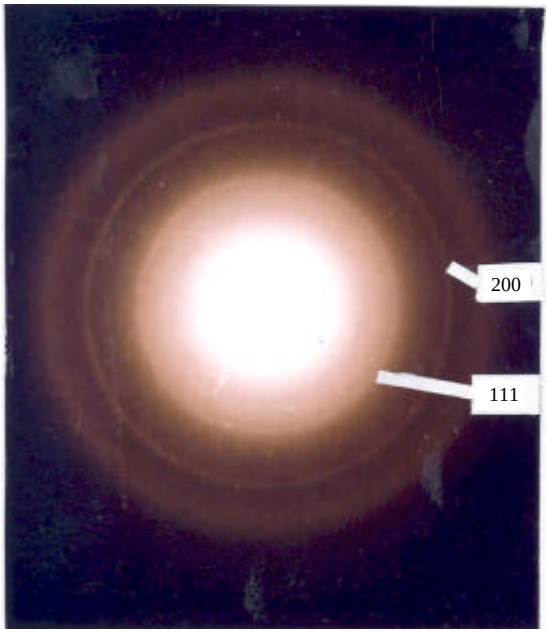

Fig. 3: Electron diffraction image of platinum nanoparticles (adsorbed on alumina) prepared in microemulsion ($C_{12}E_4$+water+C_6H_{12}) (W = 10)

The catalytic efficiency of the nanostructures material (Pt adsorbed on alumina) was examined by carrying out the oxidation reaction of CO to CO_2 taking each time 0.1 g of the prepared catalyst in the reactor. The plot of the fraction of inlet-CO concentration at the reactor outlet against temperature (°C) (Fig. 4). The catalytic activity of the nanoparticles has been ascertained in terms of the observed temperature at which 50% of CO is converted to CO_2 and thus lower the temperature of conversion higher is the catalytic efficiency. Using pure alumina as catalyst 50% conversion of CO to CO_2 occurs at 325°C (Yadav *et al*., 2003). Figure 3 shows that the conversion of CO to CO_2 using platinum

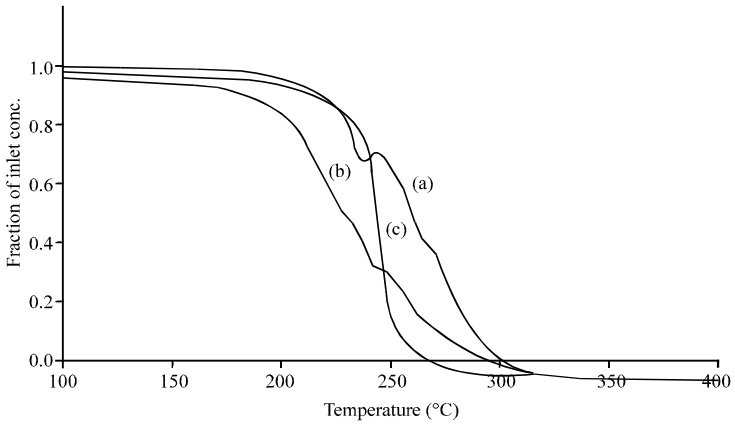

Fig. 4: Plots of fraction of iulet concentration of CO at the reactor outlet as a function of temperature. Platinum nanoparticles catalyst synthesized in microemulsion: (a) ($C_{12}E_4$+H_2O+C_6H_{12}) (W = 10); (b) ($C_{12}E_4$+ H_2O + C_6H_{12}+ PVP (0.5%) (W = 10) and (c) ($C_{12}E_4$+ H_2O + C_6H_{12}+ PEG (0.5%)) (W = 10)

nanoparticle catalysts prepared in microemulsion without a polymer as stabilizer occurs at 262°C. However, Platinum nanomaterial synthesized using 0.5% PEG (w/v) as stabilizer in the microemulsion such conversion occurs at 255°C. Using 0.5% PVP (w/v) in the microemulsion yielded the metal nanomaterial which exhibited even better catalytic efficiency since the conversion of CO to CO_2 occurred at a further lower temperature (245°C). The observed higher catalytic activity of the nanoparticles obtained in the presence of polymer compared with those prepared in microemulsion without a polymer may result from the tempelating action of polymer in the production of the platinum nanomaterials. In this respect structural characteristics of PVP is considered to play a better role. The results of the present study reveals that the use of Pt/Alumina interface as catalyst for converting CO to CO_2 is quite effective in lowering the conversion temperature. However, further investigations are needed to explore whether this catalyst system also suits for the degradation of residual hydrocarbons and oxides of nitrogen and sulphur in the automotive exhaust system.

CONCLUSIONS

Platinum nanomaterials have been synthesized in water-in-oil microemulsion ($C_{12}E_4$ + C_6H_{12} + H_2O) in the absence and presence of PVP and PEG. The nanostructures are characterized by electron diffraction, XRD and TEM techniques. The catalytic activity of the nanomaterials is monitored in terms of CO to CO_2 conversion reaction as a function of temperature. The nanoparticles synthesized in the microemulsion containing PVP exhibit higher catalytic efficiency compared with those prepared in the microemulsion without a polymer and PEG + microemulsion systems.

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