Synthesis of nanosized platinum based catalyst using sol-gel process

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Abstract. The nano-sized platinum based catalysts using high surface area silica support have been prepared by sol-gel method. Tetramethoxysilane (TMOS) diluted in methanol was hydrolyzed to form a porous silica gel. Platinum (2%) was loaded at sol state using platinum chloride solution. After gelation, the solvent from the gel pores was extracted at ambient temperature which resulted in porous silica matrix incorporated with nanosized platinum. X-ray diffraction studies indicated the presence of elemental platinum in the silica-platinum composites. Transmission electron microscopy of the platinum–silica composites revealed that nanosized platinum particles of about 5-10 nm are homogeneously dispersed in silica matrix. Chemisorptions studies showed high dispersion (more than 50%) of platinum on silica support with specific surface area of 400 m²/g which puts them as promising candidates as catalyst in heterogeneous reactions.

Keywords: Sol-gel technique, Mesoporous silica, Platinum catalyst, Chemisorption

1. Introduction
The platinum (Pt) based catalysts are highly applicable as catalyst in heterogeneous (solid-gas) reactions. The hydrogen isotope exchange reaction between hydrogen gas and water using Pt catalyst are exceedingly favourable to remove tritium from water [1] in nuclear industries. For such applications, the major requirements of catalyst are large surface area and high dispersion of active sites. The high surface area can be achieved by reducing the particle size of active catalyst to nanometer scale. The high dispersion requirement can be met by choosing proper support matrix for dispersion of catalyst material. The hydrophobic nature of the support matrix is also a critical requirement [2]. The sol gel process is a promising method for preparation of nano-sized particles that can be homogeneously dispersed on gel matrix, mostly of silica. The sol-gel process allows the preparation of metal nanoparticles in oxide matrices with narrow particle size distributions and adjustable metal loadings [3]. In the present works, we developed a method to obtain the nano sized platinum dispersed on porous silica matrix prepared by sol-gel process. The micrographs obtained from transmission electron microscopy showed formation of 5-10 nm platinum particles where as the chemisorptions studies revealed high dispersion of platinum in silica matrix.

2. Experimental
A platinum-silica nano composite was prepared by sol-gel process [4]. To prepare silica gel, tetramethoxysilane (TMOS) diluted in methanol was hydrolysed. The molar ratio of acetone/TMOS

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was kept as 12. The platinum solution (PtCl₄) was added as Pt source to the silicate solution. The molar ratio of PtCl₄ to TMOS was chosen so as to achieve 2% platinum loading in silica-platinum composite. Methyltrimethoxysilane (MTMS) was added as hydrophobic reagent to this solution in molar proportion of TMOS/MTMS as 4. The gelation of silicate solution was accelerated using ammonium hydroxide (0.5 M NH₄OH). After gelation, the solvent from the gel pores was extracted at ambient temperature and pressure which resulted in porous silica matrix incorporated with nanosized platinum.

The crystalline data for silica/platinum composite was obtained on a Philips X-ray diffractometer using a PW 1710 goniometer (CuKα, 30 kV, 20 mA). For transmission electron microscopy (TEM), the powdered sample diluted in methanol was dispersed on a carbon coated copper grid of 200 mesh size. Electron micrographs were obtained using JEOL 2000FX transmission electron microscope operating at 160 kV. Hydrophobicity of the silica support system was evaluated by using Karl-Fischer technique [5]. Chemisorptions studies on the samples were carried out using TPDRO 1100, Thermo Scientific, Italy. Samples were pretreated by heating in a stream of Argon (20 ml min⁻¹) for 2 h at 300°C and then cooled to room temperature. Helium with 5% H₂ was passed over the sample. The catalysts were then exposed to pulses of H₂ gas. From the amount of chemisorbed H₂ the percentage of the accessible Pt atoms has been calculated.

3. Results and discussion
The x-ray diffraction spectrum of platinum-silica nanocomposite with 2 % platinum loading is shown in figure 1. The broad peak around 22° is assigned to amorphous silica. The formation of nanoparticle of platinum is indicated by the characteristic peaks at 2θ values of 40, 46 and 67° in the diffractogram obtained by using Cu-Kα (1.54 Å) x-rays. The peaks could be assigned to 111, 200 and 220 plane, respectively [3]. The average metal particle size calculated from the width of the [111] peak using Scherer equation is 3 nm.

![Figure 1 X-ray diffractogram for Pt-silica nanocomposite.](image)

Transmission Electron Microscopy (TEM) image (figure 2 a) shows that nanosized platinum particles of about 5-10 nm are homogeneously dispersed in silica gel matrix. The selected area electron diffraction (figure 2 b) obtained for the platinum-silica composite confirmed the presence of nanocrystalline platinum. The inter planer d-spacing were deduced from the concentric rings and were attributed to platinum.
The Karl-Fischer titration method showed only 0.08% water adsorption for the Pt-silica nanocomposite sample that was placed on water for 3 days before measurement. It indicated super-hydrophobic nature of the silica support system [5].

The catalytic properties of the nanocomposite are tested through exposure to hydrogen gas. Pulse studies performed on the catalyst to evaluate the Pt dispersion on the support. The typical pulse profile of adsorbed H₂ on the nanocomposite is shown in figure 3.

The specific surface area of the Pt-silica nanocomposite was found to be 400 m²/g where as the surface area of metal was found to be 140 m²/g. Chemisorptions studies conducted using H₂ showed 50.6 % of accessible platinum atoms on the silica matrix that indicate high dispersion of platinum on silica support.

4. Conclusions
The nano sized platinum particles have been prepared by sol gel method using silica support. The high dispersion (50.6 %) of Pt nanoparticles has been achieved on hydrophobic silica gel matrix with
surface area of 140 m$^2$/g for the metal. The well dispersed Pt nanoparticles on silica support system could be potential catalyst in heterogeneous reactions.

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**References**
[1] Izawa H, Isomura S and Nakane R 1979 *Journal of Nuclear Science* **16** 741
[2] Choi H J, Lee H, Kim K R and Ahn D H 2002 *J. Ind. Eng. Chem.* **8** 586
[3] Lembacher C and Schubert U 1998 *New J. Chem.* **22** 721
[4] Ingale S V, Wagh P B, Tripathi A K, Kamble V S, Rataneshkumar, Gupta S C 2011, *Journal of Porous Materials* **18** 567
[5] Wagh P B, Ingale S V and Gupta S C 2010 *J. Sol-Gel Sci. Technol.* **55** 73