Electronic Supplementary Information

Effect of preparation conditions on structure-electrical property relationship with catalytic performance of silica-supported Pt nanoparticles

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Experimental Section

All the chemicals used were of analytical grade, of 99.9 % purity. Hexa chloroplatinic acid [$H_2PtCL_6.6H_2O$] (Merck) was used as a precursor for preparation of Pt nanoparticles. Sodium hydroxide (NaOH), ethylene glycol ($C_2H_6O_2$), hydrazine monohydrate ($N_2H_4.H_2O$), n-hexane, cyclohexane and ethanol (absolute) were used as received. In the typical synthetic procedure, a calculated amount of SiO_2 support was impregnated with the solution of $H_2PtCl_6.6H_2O$ of certain concentration in deionized water such that the loadings of Pt were 0.3, 0.6 and 0.9 wt %. The reduction process to get Pt nanoparticles was proceeded through two different techniques. In the microwave-assisted solution (MAS) method, EG (50 ml) with drops of NaOH was added first to the solutions, after which 5 ml of hydrazine monohydrate were added drop wisely. The mixture was then irradiated in a commercial microwave oven (Kenwood Model MW 867, 1100 W, 2.45 GHz, λ =12.2 cm, with electronic digital system) for 2 minutes. The filtered solids were washed with deionized water and acetone for several times and then washed with absolute ethanol. Finally, the obtained catalysts were dried for 24 hr at 70° C in a vacuum oven. In the rotary chemical evaporation (RCE) method, EG (50 ml) was added to the solution mixture heated at 60° C for 30 min in an oil bath (SB-1000), designed for the rotary evaporator, EYELA Model N1001 S-W, in a standard 1000 ml pear shaped flask. Sodium hydroxide solution was added drop wisely. When the color of the solution changed from dark yellow to light yellow, the temperature of rotary evaporator (with standard diagonal condenser glassware nozzle OD 3/8'' (10 mm), equipped with a digital temperature display) was raised to 75° C and kept for 20 min. 5 ml of hydrazine hydrate was added drop wise and the mixture was kept at 75°C for 1 h. The precipitates were washed with copious de-ionized water and acetone for 3 times, then with absolute ethyl alcohol and dried at 70° C for 24 h in a vacuum oven. Several characterization techniques were adopted such as N_2-adsorption-desorption, H_2-chemisorption, DSC/TGA, XRD and TEM. The A.C. electrical conductivity measurements were displayed in the applied frequency range, 42 Hz – 100 kHz, at room temperature (20° C) and correlated with metal dispersions and catalyst activities. The catalytic performances of different catalyst samples were assessed during ethanol oxidation and cyclohexane dehydrogenation, using micro-catalytic pulse-flow technique at different operating conditions.

For testing the reproducibility of results from the applied reduction techniques, some catalyst samples of different Pt loadings were prepared twice. In guide experiments, 1g batches were prepared to be compared with the 5g batch prepared and used in the experimental part of the present work, under the same synthesis conditions. Selected physicochemical characteristics

were compared to check the reliability of reduction method used, namely, through XRD and TEM investigations.

For 0.6% Pt-SiO_2 reduced by MAS method, both the samples (1g batch and 5g batch) showed the same broad peak located at 2θ of 15-30^o (Fig S1), exactly as the other samples from 5g batch, viz., with 0.3% and 0.9% Pt loadings.

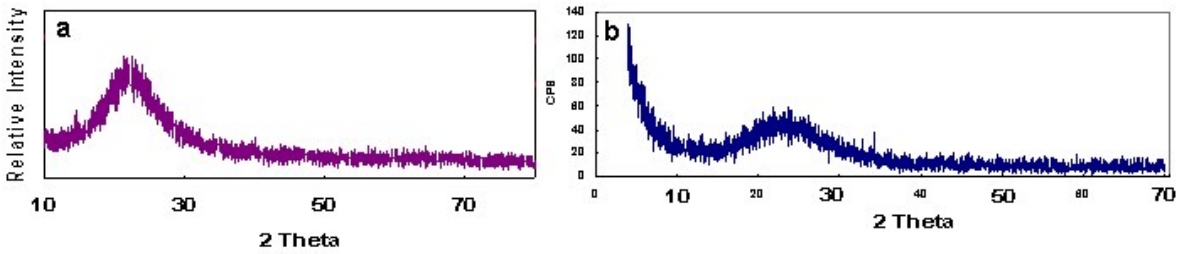

Fig.S1 XRD pattern of 0.6 Pt-Si samples reduced by MAS method: (a) from 5g batch (as those used in the present study for different Pt loading %), (b) from 1g batch for check.

Again, the 0.6% Pt-SiO_2 samples reduced by MAS method from both 1g batch and 5g batch showed similar TEM images as depicted in Fig. S2. The average particle size for the sample from 1g batch was 5-7 nm and that for the sample from 5g batch was 4-10 nm.

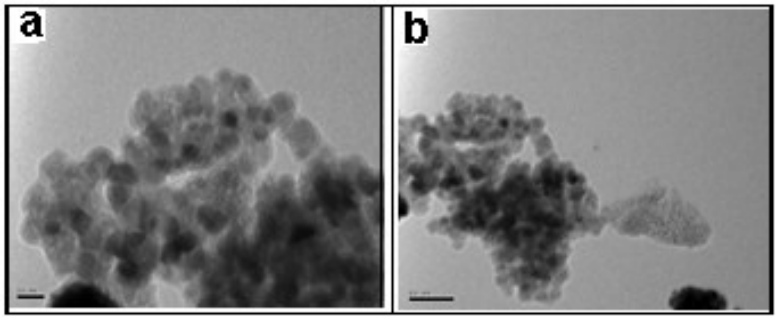

Fig.S2 TEM images of 0.6 Pt-Si samples reduced by MAS method: (a) from 5g batch (as those used in the present study), (b) from 1g batch for check.

Also, for 0.9 % Pt-SiO_2 reduced by RCE method, both the samples (1g batch and 5g batch) showed similar TEM images as depicted in Fig. S2. The average particle size for the sample from 1g batch was 3-7 nm and that for the sample from 5g batch was 3-5 nm.

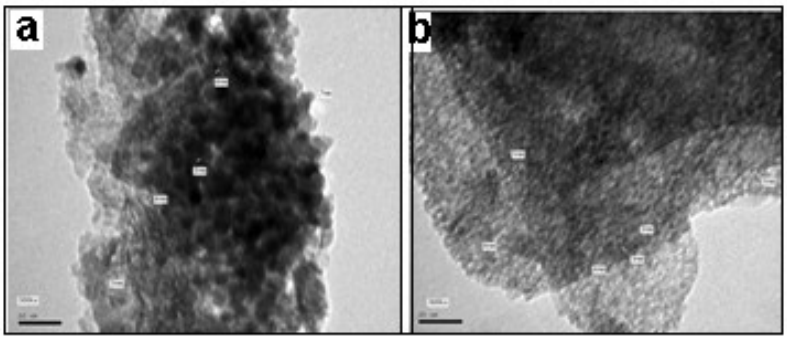

Fig.S3 TEM images of 0.9 Pt-Si samples reduced by RCE method: (a) from 1g batch, (b) from 5g batch for check (as those used in the present study).

Generally, this supporting information may confirm the reliability of the synthesis techniques applied in our present work, in particular the reduction methods used, either MAS or RCE. Suitability of using microwave irradiation, with optimized conditions, to give concordant results with those obtained by commonly used rotary chemical evaporation is also revealed.