

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: S. A. Hassan, H. M. Gobara, M. M. Gomaa, R. S. Mohamed and F. Henry, *RSC Adv.*, 2015, DOI: 10.1039/C5RA08116E.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

Can microwave assisted in situ reduction of supported Pt nanoparticles be challenging with chemical method in controlling the dispersion profilecatalytic performance relationship

Salah A. Hassan¹, H. M. Gobara^{2*}, M. M. Gomaa³, R. S. Mohamed², F. H. Khalil²

¹ Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt. ² Catalysis Department, Refining Division, Egyptian Petroleum Research Institute, 1 Ahmed El-Zomor St., Nasr City, 11727, Cairo, Egypt. ³ Geophysical science Department, Physics building, National Research Center, Dokii 12311, Cairo, Egypt.

* Corresponding author; email: hebagobara@ymail.com , Tel: +2(02) 01223898196, +2(02) 01091446345, Fax: +2(02)227727433.

Abstract

In this study, Pt (of 0.3, 0.6 and 0.9 wt % loadings) was supported on mesoporous silica surface via microwave-assisted solution (MAS) method or rotary chemical evaporation (RCE) method in the in situ reduction step. The as-synthesized Pt nanocatalysts were characterized through XRD, XRF, TGA/ DSC, TEM, N2-adsorption-desorption, H2-pulse titration and electrical conductivity techniques. The samples prepared by MAS method exhibited higher surface area and a better dispersion profile of Pt NPs, of average sizes not exceeding 10 nm with increasing the Pt loading. In contrast, although RCE method showed higher efficacy in decomposing the used precursor, uneven distribution of larger Pt nanoparticles (\geq 33 nm) was displayed. Electrical properties in terms of AC conductivity and dielectric constant confirmed the enhancement of even distribution of smaller Pt NPs with higher concentration of grain boundaries affected by microwave electromagnetic radiations. Highly mobile electrons and lattice vibrations (phonons) were favored, as compared with aggregated NPs produced during RCE method. The TOF values calculated for reactions to selectively produce ethylene (from ethanol) or benzene (from cyclohexane) decreased with Pt loadings on catalyst samples synthesized by MAS method. The highly dispersed NPs (of 3-7 nm) seemed to be responsible of the activity in both reactions, tending probably to be structure insensitive. However, samples reduced by RCE method, with enlarged average sizes of surface Pt NPs (approaching 15.5 nm), exhibited increasing TOF values with Pt loading, i.e., turning the reactions most probably to be structure sensitive.

Keywords: Pt-SiO₂ nanocatalysts; Microwave-assisted solution method; Rotary chemical evaporation method; Dispersion profile; Dielectric properties; Catalytic performances

1. Introduction

Transition metal nanoparticles supported on metal oxides have been used as catalysts for a variety of organic reactions, including hydrogenation, dehydrogenation, oxidation, etc. They have advantages such as enhanced activity, selectivity and dispersion of metallic species during immobilization on support surface. Metal oxides supports usually exhibit high surface areas, high thermal stabilities and organized pore structures. Commonly used supports are alumina [1] zeolite [2], titania [3], carbon [4] and silica [5]. Of these supporting materials, silica has a potential to be used in a wide variety of applications ranging from microelectronics to medical applications [6]. The silica supports used include silica gel [7], silica monoliths [8], mesoporous silica [9] and others.

Supported nanocatalysts are typically prepared in two steps. In the first step, the loading of metal precursor on support surface can be achieved by several techniques, including

impregnation, where dispersion property depends on the metal, metal loading and support, deposition/precipitation or co-precipitation, where metal dispersion depends on the nature of support, solution pH and concentration of the precursor solution [10], and grafting involving formation of covalent bond between the metal precursor and the support functional groups [11]. The second step includes calcination and/or reduction at different conditions, which controls the metal-support interaction, mode of metal dispersion and consequently the average particle size as well as the dispersion behaviour-catalytic performance relationship [12]. The two steps together significantly affect the overall properties of the resultant catalyst.

Among the applied catalyst preparation techniques, microwave-assisted irradiation is now growing in popularity, as a time saving and energy efficient process [13]. In this technique, it is important that the synthesis medium has the ability to absorb the electromagnetic radiations and to efficiently convert them to heat. This property is related to the material's loss factor or loss tangent [14]. Ethylene glycol (EG), frequently used in microwave irradiation, has a high loss tangent of 1.35 at 2.45 GHz, which is a high value when compared to the other solvents [13]. It serves not only as the reducing agent but also provides the heating environment.

In this work, a comparative study is presented to follow the effect of preparation conditions to optimize the dispersion properties of Pt nanoparticles / SiO_2 , as synthesized by impregnation technique and via applying microwave-assisted solution method (MAS) or rotary chemical evaporation (RCE) method in the *in situ* reduction step. The comparative study was extended to include the electrical properties within the various characteristics in relation to the catalytic performances of the studied systems in ethanol and cyclohexane conversions.

Electrical properties of such highly dispersed systems and related mesoporous structures have attracted the attention of several researchers, as the understanding of charge transport mechanism in support/guest materials is important both from fundamental and technological points of view. Dielectric measurements are acceptable means for studying the dynamic properties (capacitance, conductance, permittivity and loss factor) of dielectrics. The previous works [15, 16] have focused on mobility of the exchangeable cations (Pt and Ni) loaded on different supports. Recently, the enhancement of electrical conductivity of the hybrid prepared from Pt NPs and reduced graphine oxide (rGO) using the aniline stabilizer was reported to originate from the small particle size, uniform dispersion of Pt NPs and good interfacial interaction between the Pt NPs and r-GO hybrid [17]. In the present study, the A.C. conductivity and dielectric constants were studied in the frequency range from 42 Hz to 5 MHz, at 300 K and 1 V, with an attempt to explore how the charge transport and relaxation can be affected by the support/guest interaction raised in both synthesis methods applied.

2. Experimental

2.1. Materials

Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36

All the chemicals used were of analytical grade (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 (C₂H₆O₂, EG), hydrazine monohydrate (N₂H₄.H₂O), cyclohexane and ethanol (absolute) were used as received.

2.2. Preparation of nanocatalysts

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 %. Two different reduction techniques were applied to get the Pt nanoparticles, namely;

i) In the microwave-assisted solution (MAS) method, EG (50 ml) with drops of NaOH was added first to the impregnated Pt precursor solution, after which 5 ml of hydrazine monohydrate were added drop wise. The mixture was then irradiated for 2 min in a

RSC Advances

commercial microwave oven (Kenwood Model MW 867, 1100 W, 2.45 GHz, $\lambda = 12.2$ cm, with electronic digital system). The filtered solids were washed with deionized water and acetone for several times and then washed with absolute ethanol. Finally, the obtained catalyst samples were dried for 24 h at 70 °C in a vacuum oven.

ii) In the rotary chemical evaporation (RCE) method, EG (50 ml) was added to the impregnated Pt precursor solution 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 wise. When the colour 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 precipitate was 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.

2.3. Physicochemical Characterization

The textural characteristics of the prepared nano-catalysts were investigated by the aid of N_2 adsorption-desorption isotherms measured at -196° C using a NOVA 3200 apparatus, USA. All samples were pre-treated under vacuum (10⁻⁴ Torr) at 300° C for 24 h. Surface areas (S_{BET}) were calculated from the adsorption isotherms by applying BET equation using multi–points method at relative pressure P/Po range 0.05 - 0.3. Pore size distribution was estimated BJH method from the desorption branch of the isotherms.

The powder X-ray diffraction (XRD) patterns were recorded adopting a Brucker D8 advance X-ray diffractometer, using Cu–K α radiation (λ =1.5418 Å) with 30 mA and 40 kV in the 2 θ from 10 to 80° range with a scan rate of 10° min⁻¹.

The elemental composition of the samples was determined by X-ray fluorescence (XRF) spectrometry in a Panalytical AXIOS PW4400 spectrophotometer with Rh tube as source of radiation. The measurements were performed onto pressed pellets containing 6 wt % wax.

Thermal gravimetric and differential scanning calorimetric (DSC-TGA) analyses were performed using simultaneous DSC-TGA devise of model SDTQ 600, USA, under N_2 atmosphere, with a heating rate of 10° C min⁻¹.

The degree of surface dispersion and average size of supported Pt nanoparticles was assessed through H₂-chemisorption. The sample was maintained at 300° C for 2 h, flushed in a pure dry nitrogen gas flow (20 cm³ min⁻¹) for 30 min and then cooled to room temperature. Thereafter, the sample was subjected to hydrogen chemisorption on Chembet 3000 apparatus, Quantachrome USA, using a pulse titration (pulse volume = 0.1 cm³) and 10 % (v/v) H₂/N₂. The hydrogen uptake was expressed in μ LH₂ at STP per g of catalyst.

The morphology of different samples were investigated by the aid of high resolution transmission electron microscope, model JEM 2100 (JEOL, Japan). It offered high resolution electron imaging up to 0.143 nm and magnification as high as 1.5 million times.

2.4. Catalytic activity measurement

Catalytic activity of SiO₂ and supported (Pt-Si) nanocatalysts were tested in cyclohexane and ethanol conversions as two model reactions using a micro catalytic pulse reactor. The reactor effluent was passed through a chromatographic column for separation and determination of the products using flame ionization detector (FID) connected to computerized data acquisition station. The column of 200 cm length and 0.3 cm internal diameter was used containing acid-washed PW chromosorb (60-80 mesh size) loaded by 15% by weight squalane. The reactions were carried out under atmospheric pressure in the temperature range, $250 - 450^{\circ}$ C. Hydrogen

(8)

flow rate was kept constant at 50 ml min⁻¹. Prior to catalytic activity runs, the reduced catalyst samples were heated in H_2 flow for 2 h at 450° C for activation. Few doses of reactants were injected first to reach the steady state of the reaction. The chromatographic column temperature was adjusted and controlled at 50° C.

The catalytic activity experiments for ethanol and cyclohexane conversions were expressed in the terms of yield, total conversion, % selectivity and the turnover frequencies calculated as follows:

Ethanol or cyclohexane conversion (wt %) = Σ yield % of each component in the products Component yield (wt %) = Quantity of the component / Total quantity of the produced components Fractional selectivity of each component (wt %) = Yield (wt %) / total conversion X 100. Turnover frequencies = moles of product produced (or substrate consumed)/ surface metal per unit time

2.5. Electrical properties measurement

The geometry (area and thickness) of the samples for electrical measurements was chosen to reduce errors due to stray capacitance. The sample faces were polished to be parallel using Hioki 3522- 50 LCR Hitester Impedance Analyzer. Samples were collected to cover all Jurassic formations present in the area. Data were measured in the frequency range from 42 Hz to 5 MHz. The samples were connected to non-polarizing electrodes (Cu/CuSO₄) [15, 16] and the oscillation amplitude was set at 1 volt (small signal).

Electrical properties of various samples under study could be expressed in either the series or parallel configuration. The measured parameters involved parallel capacitance (C_p) , conductance (G_p) and series impedance (Z) at different frequencies. The complex relative dielectric constant ε^* could be expressed as: $\varepsilon^* = \varepsilon' - i\varepsilon''$ (6),

where, the real part of the complex relative dielectric constant (ε') before correction is $\varepsilon' = C_p d / \varepsilon_0 A$ (7)

and the imaginary part of the complex relative dielectric constant (ε ") is

$$\varepsilon'' = G_p d / \omega \varepsilon_0 A$$

A is the cross-sectional area of the sample, d is its thickness, ε_0 is the permittivity of free space (8.85×10⁻¹² F/m) and ω is the angular frequency. The conductivity was thus calculated from the following equation:

$$\sigma' = G_p(d/A) = \varepsilon'' \omega \varepsilon_0 \tag{9}$$

where, σ' is the real part of the conductivity.

The measurements were performed in an isolated chamber at room temperature ($\sim 27^{\circ}$ C) and atmospheric relative humidity of ($\sim 40\%$).

3. Results and Discussion

Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36.

3.1. Physicochemical characteristics of various Pt/SiO₂ nanocatalyst samples synthesized through different reduction methods

3.1.1. XRD and XRF analyses

The XRD patterns obtained for silica support and supported Pt/SiO_2 nanocatalyst samples of different Pt loadings, viz., 0.3, 0.6 and 0.9 wt %, prepared by the MAS reduction method are shown in Fig. 1(a). The corresponding patterns of the same catalyst samples prepared by RCE method are shown in Fig. 1(b). It is obvious that the amorphous pattern of SiO₂, characterized by the broad peak located at 20 of 15-30° [22], is maintained in all studied catalyst samples by varying the reduction methods. Moreover, no diffraction lines could be observed for Pt phases, referring to the well dispersed state of Pt NPs of average sizes less than 30 Å in all cases.



Fig.1: XRD patterns of (a) parent silica support and various samples of Pt/SiO₂ nanocatalyst synthesized via MAS reduction method and (b) the corresponding samples prepared by RCE method

On the other hand, the atomic percentages of loaded Pt determined by XRF in all catalyst samples synthesized by the mentioned reduction methods (MAS and RCE) are included in Table 1. The obtained atomic percentages, normalized as a ratio to SiO₂ rather than to the other components of the catalyst system, are very close to the targeted ratios for this study. However, the relatively lower ratios of Pt, than the nominal ones, exhibited in case of RCE reduction method seems to be related to the type of longer term rotary chemical treatment. This assists the efficient decomposition of the precursor; deeper penetration of a fraction of Pt NPs in pore system and some loss upon evaporation and purification. During MAS reduction, exposing the synthesis system to electromagnetic radiations, even for only short time not sufficient for complete decomposition of Pt precursor, seems to expel a fraction of Pt out of pores to the external surface, with some loss of magnetic SiO₂ NPs (i.e., leading to some relatively higher Pt ratios than the nominal ones). In all cases, some sort of strong interaction between Pt and SiO₂ support seemed to exist without detectable leaching of Pt species.

3.1.2. Textural investigation

The N₂ adsorption-desorption isotherms over the surface of silica support and various samples of supported Pt/SiO₂ prepared by MAS reduction method as well as their pore size distribution curves are illustrated in Fig. 2 (a and b). Also, the measured isotherms and pore size distribution curves over the catalyst samples of the same Pt loadings prepared through the RCE method are shown in Fig. 2 (c and d). The isotherms obtained for the as-synthesized catalyst samples by both methods are similar in behavior to that of silica support, probably due to the nanosized metal particles and/or their high dispersion. All the presented isotherms are of type IV, characteristic mainly of the mesoporous silica [18], being associated with hysteresis loops of H2 type in the relative pressure (p/p₀) range of 0.4 - 0.8, usually related to the ink-bottle pores with narrower orifice of the border inner parts [19].

Table 1 summarizes the different surface data derived from the adsorption isotherms. It is clear that the surface area of pure silica support has suffered a marked decrease by loading Pt nanoparticles, reduced by either MAS or RCE methods. The catalyst samples synthesized by MAS reduction method had relatively higher surface areas, especially for diluted samples, as compared with those samples synthesized by RCE method. Although the pore volume exhibited only slight changes in both sets of synthesized nanocatalysts, the average pore radii showed a considerable decrease, especially for lower Pt loadings, viz., 0.3 and 0.6 wt %,

(becoming more pronounced with MAS reduction) most likely due to incorporation of a fraction of Pt nanoparticles near the orifices of the silica pore system.

For the 0.9 Pt-SiO₂ sample prepared by MAS method, a slight increase in pore volume with almost retained pore radius as that of pure silica may suggest the transfer of a fraction of Pt nanoparticles to the top surface. In contrast, for the same catalyst sample of 0.9 % Pt, prepared by RCE method, the increase in surface area with nearly the same pore size parameters as 0.3Pt-SiO₂ and 0.6Pt-SiO₂ samples may be related to deeper incorporation of Pt nanoparticles in SiO₂ pore system.

As in pure silica support, relatively narrower unimodal pore size distributions (PSD) of most probable hydraulic pore diameter D = 3.60 nm were shown for the catalyst samples synthesized by MAS method (Fig. 2, b). Their population seemed to decrease with the increase in metal loading, due probably to the transfer of some of Pt NPs out of the pore system. However, for catalyst samples synthesized by RCE method, the slightly broadened PSD curves were shown with smaller most probable hydraulic pore diameter D = 3.39 nm.



Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36

Fig. 2: N_2 adsorption-desorption isotherms for bare SiO₂ support and Pt/SiO₂ nanocatalysts synthesized by: (a) MAS method and (c) RCE method, as well as the pore size distribution curves (PSD) of SiO₂ support and Pt/SiO₂ nanocatalysts synthesized by: (b) MAS method and (d) RCE method.

Table 1 Surface parameters of SiO_2 and various $Pt-SiO_2$ nanocatalyst samples prepared by MAS and RCE method and atomic percentages of supported Pt determined by XRF in all cases.

Catalyst sample	Pt loading (wt %) ^a	$\frac{\mathbf{S}_{\mathbf{BET}}}{(\mathbf{m}^2 \mathbf{g}^{-1})}$	$\frac{\mathbf{V}_{\mathbf{P}}}{(\mathrm{cm}^{3}\mathrm{g}^{-1})}$	r _p (nm)
SiO ₂		444.0	0.430	8.52
Pt/SiO	2 samples synt	hesized by	MAS met	nod
0.3 Pt-Si	0.341	352.5	0.427	3.88
0.6 Pt- Si	0.610	362.2	0.429	3.94
0.9 Pt- Si	0.913	356.1	0.479	8.26
Pt/SiC	2 samples synt	thesized by	y RCE meth	nod
0.3 Pt-Si	0.289	335.0	0.406	4.74
0.6 Pt- Si	0.591	265.2	0.384	4.19
0.9 Pt- Si	0.897	382.4	0.443	4.39

^a Wt % of Pt from elemental analysis by XRF

3.1.3. Platinum dispersion profile in various Pt/SiO₂ nanocatalyst samples

The degrees of surface dispersion of Pt in the various Pt/SiO_2 samples, synthesized via MAS and RCE reduction methods, were evaluated from the H₂ chemisorption data, summarized in Table 2, assuming the adsorption stoichiometry of H: Pt = 1: 1. It is clear that the degree of Pt dispersion decreased by increasing the Pt loading in both the applied reduction methods. The dispersion values (D) were higher by using MAS method, where the dispersion profile seemed more regular. The dispersion parameters for higher Pt loadings (0.6 % and 0.9 %) were better by applying MAS method than those obtained by RCE method, i.e., more fraction of exposed surface atoms of Pt (cf., smaller average particle sizes, a_e in nm, and higher surface areas of supported Pt, S_{Pt} , m^2g^{-1}). For diluted catalyst samples (of 0.3 % Pt), the dispersion parameters, D, a_e and S_{Pt} , obtained by using RCE method, were comparable with, or even more favorable than those parameters resulted in MAS method.

Catalyst	Degree of	Av. Particle	Metallic surface			
sample	Dispersion	size (a _e , nm)	$(\mathbf{S}_{\mathbf{Pt}}) (\mathbf{m}^2 \mathbf{g}^{-1})$			
	(D)					
Pt/S	Pt/SiO ₂ samples synthesized by MAS method					
0.3 Pt-Si	0.763	3.71	754.3			
0.6 Pt- Si	0.607	4.66	599.9			
0.9 Pt- Si	0.368	7.70	363.3			
Pt/SiO ₂ samples synthesized by RCE method						
0.3 Pt-Si	0.966	2.30	725.2			
0.6 Pt- Si	0.316	15.50	474.4			
0.9 Pt- Si	0.129	15.50	358.5			

Table 2 Degree of Pt dispersion (D), average size of Pt nanoparticles (a_e) and metallic surface area of supported Pt nanoparticles in Pt/SiO₂ catalysts synthesized by MAS or RCE method

3.1.4. Thermal analysis

Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36.

The TGA and DSC analyses of various Pt/SiO₂ nanocatalysts synthesized by MAS or RCE in-situ reduction methods were performed at temperatures ranging between 25 to 1000° C under N₂ atmosphere (Fig. 3, a-d). Almost the same thermal trend was displayed in both cases, exhibiting reasonable thermal stability up to 1000°C. As seen in this figure, the main weight loss was occurred below 100° C accompanied with an endothermic peak representing the removal of physically adsorbed water from the catalyst surface. The intensity of this endothermic peak becomes more pronounced with increasing the metal loading, especially in the 0.9 Pt –Si sample reduced by RCE method. Furthermore, the TG curves for the diluted samples (0.3Pt and 0.6 Pt loaded samples) reduced by MAS method showed a slight weight loss in the second step in the range, >200 – 550° C. This step seemed to be linked with the progressive decomposition of the residual precursors, probably without heat changes. Moreover, the lower losses in weights in this region for the samples prepared by RCE method (2.1 % vs. 5.3 % in MAS method) can be related to the relatively higher efficacy of this method in decomposing the used precursor.



Fig. 3: TGA (a) and DSC (b) of SiO_2 support, Pt/SiO_2 nanocatalysts with different Pt loadings synthesized through MAS reduction method. TGA (c) and DSC (d) of Pt/SiO_2 nanocatalysts synthesized through RCE method

3.1.5. Morphological investigation

The TEM images obtained for pure SiO_2 support and the various Pt/SiO_2 nanocatalyst samples (of 0.3, 0.6 and 0.9 wt % Pt) synthesized via MAS reduction method are depicted in

RSC Advances

Fig. 4. For silica support, the image (a) shows very fine, homogenous and well distributed nanoparticles of an average size ≤ 2 nm. On the other hand, for the diluted catalyst sample (of 0.3 % Pt), image (b) reveals even dispersion of surface Pt nanoparticles with average sizes ≤ 3 nm. By increasing the Pt loading to 0.6 wt %, the Pt nanoparticles approaching average sizes of 5-6 nm seem to be embedded in the nanosilica matrix (image c). By further increasing the Pt loading to 0.9 wt %, an increase in Pt particle sizes is occurred (image d), but still not exceeding 10 nm. This sample exhibited a distinguished dispersion profile, compared with the other samples in this series, which may run in harmony with the suggestion of transfer of a fraction of incorporated Pt nanoparticles in silica pore system to top surface of the support (cf. textural results).

As well, the TEM images of the studied catalyst system with the same Pt loadings synthesized by RCE method are represented in Fig. 5. The 0.3% Pt/SiO₂ sample shows homogeneously distributed larger Pt particles of average sizes in the range of 18-25 nm (image a). By increasing the Pt loading to 0.6 %, some enlarged particles of average sizes \geq 33 nm are occurred (image b), as embedded in silica matrix in less homogeneous surface distributions. For the 0.9 % Pt-S, the well dispersion of Pt nanoparticles with average particle sizes of 3-5 nm in some sheet structure becomes evident (image c). This observation may confirm the deeper incorporation of Pt nanoparticles in silica pore system, associated with some restructuring effect (cf. textural results).

Generally, it is clear that the applied MAS reduction method achieves more organized distribution of less sized Pt nanoparticles on the outer surface of silica support, compared to the RCE method.

Reproducibility of characterization results obtained for the samples produced by applying both MAS and RCE methods was inspected as described in the electronic supporting information (Fig S1 and Fig S2).



Fig. 4 TEM images of parent silica support (a) and various Pt/SiO_2 nanocatalyst samples of: (b) 0.3 wt % Pt, (c) 0.6 wt % Pt and (d) 0.9 wt % Pt, synthesized via MAS reduction method



Fig. 5 TEM images of various Pt/SiO_2 nanocatalyst samples of: (a) 0.3 wt % Pt, (b) 0.6 wt % Pt and (c) 0.9 wt % Pt, synthesized via RCE method

3.2. Electrical properties of various Pt/SiO₂ nanocatalyst samples

Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36

This part focuses on studying the A. C. electrical properties of Pt/silica nanocatalysts prepared via the two reduction methods (MAS and RCE) in the frequency range from 42 Hz to 5 MHz, at 300 K and 1 V. Assuming that Pt nanoparticles are optimally dispersed (as guest) over the surface of silica support (the host), this may give rise to electrical behavior which differs from those of the individual constituents. The obtained results showed direct dependences of the conductivity and dielectric constant on the Pt loading as well as the frequency applied, as shown in Figs. 6 and 7 for samples synthesized by RCE method and MAS method, respectively. In both cases, the conductivity increases while the dielectric constant decreases with the increase of frequency. Such changes are fast at low frequency as compared to higher frequency that may be due to the electrode polarization effects [20].

It is generally accepted that, the electrical conductivity and dielectric constant are directly related to the amount of free or bound charge carriers in the surface of the samples, as well as their mobility. The ionic conduction of samples results from the migration or exchange of cations along the channels and cavities of the grains according to an ion-hopping mechanism. The activation energy of ion hopping depends on the temperature, water content and conductor content (module) [15].

Referring to Figs 6 and 7 at low frequencies (<10 KHz), the behavior of the conductivity may reflect the production of charge carriers at the interfaces and their transportation to reach the measuring electrode where they at last discharge. At higher frequencies (> 10 KHZ), such charge carriers cannot reach the electrodes, as they are collected around grains and undergo local motion which gives rise to frequency dependent conductivity.

It is worth to recall here that such highly dispersed metal systems under study, of nano-sized particles, contain a high concentration of grain boundaries and a large internal surface in the case of porous systems, compared to the bulk material. So, the electrical conductivity is largely affected by the microstructure and mainly by the grain boundaries.

Table 3 A.C.	conductivity	σ_{AC} (at 10)0 Hz)	and	dielectric	constant	3	(at 5MHz)	for	the
Pt/SiO ₂ nanoc	atalys sample	s synthesize	ed via N	MAS	and RCE 1	reduction	me	thods		

Catalysts	σ_{AC} (S/m)	, a				
sample	100 Hz	5 MHz				
Samples synt	Samples synthesized by MAS method					
SiO ₂	3 x 10 ⁻⁸	10				
0.3Pt-Si	5×10^{-5}	12				
0.6Pt-Si	2×10^{-4}	15				
0.9Pt-Si	$1 \ge 10^{-3}$	20				
Samples syn	thesized by RO	CE method				
0.3Pt-Si	2×10^{-5}	2				
0.6Pt-Si	5×10^{-5}	9				
0.9Pt-Si	2 x 10 ⁻⁴	15				

As given in Table 3, the derived conductivity σ_{AC} (S/m) at 100 Hz and dielectric constant ϵ at 5 MHz increase with Pt loading. It is clear that the guest Pt NPs create improved electrical contact between the silica host nanoparticles. It is consequently evident that the concentration of charge carriers increases with the increase of Pt loading, probably with much transport of

RSC Advances

View Article Online DOI: 10.1039/C5RA08116E

diffused charge carriers to reach the electrodes and discharge there. Such process dominates all over the applied frequency range.

Both the electrical parameters, σ_{AC} and ϵ' , are higher for the samples synthesized by MAS reduction method, which seems to be linked with the more homogeneously distributed Pt NPs, produced with higher concentration of grain boundaries. The response of a material to electromagnetic radiation as in MAS method contains important information on highly mobile (conduction) electrons, bound (valence) electrons, and lattice vibrations, i.e., phonons. The highest conductivity and dielectric constant obtained are shown for the 0.9Pt-Si sample. Inspection of Fig 6 for pure silica and supported samples synthesized by RCE reveals that the conductivity values for pure silica exhibit nearly one slope with the frequency (~0.94). For supported Pt-SiO₂ samples, the conductivity values have two slopes; the low frequency slope is nearly zero while the high frequency slope is (~0.66). Also, the dielectric constant ϵ values

show a decreasing slope of ~ 0.46 with the frequency for the silica support and two slopes for

the supported samples (viz., ~0.46 to ~0.92 at low frequencies and ~0.06 at high frequencies). 1E-2 (S/m) 0.3 PS 0 0.6 PSP ictivity. Λ 0.9 PSP α. C.S.P.S.P 1E-3 0.9 PSP Pure Silic 1E-4 1E-5 1E-6 1E+1 1E-7 Frequency (Hz) 1E-8 1 = +0 1 1 1 1111 111111 1E+3 1E+4 1E+5 1E+6 1E+1 1E+2 1E+6 1E+1 1E+2 1E+7 1 E+ 3 1E+4

Fig.6 Conductivity and dielectric constant as a function of frequency for pure silica support as well as different samples of Pt/SiO₂ of 0.3, 0.6 and 0.9 wt % Pt synthesized via RCE method



Fig.7 Conductivity and dielectric constant as a function of frequency for pure silica support as well as different samples of Pt/SiO₂ of 0.3, 0.6 and 0.9 wt % Pt synthesized via MAS method.

From Fig. 7 illustrating the variation of conductivity and dielectric constant with frequency for the various Pt-SiO₂ samples synthesized via MAS reduction method, it can be noticed that

both parameters are markedly higher in values than those of the samples prepared by RCE method, especially at low frequencies (cf., also Table 2). At low frequencies up to 10 KHz, the conductivity shows nearly no dispersion with frequency (slope ~0.01), while at high frequencies, >10 KHz, the conductivity shows a dependence on frequency (of slope~0.6).

In conclusion, it is evident that the electromagnetic radiations in MAS method enhance the even distribution of smaller in size Pt NPs, with higher concentration of grain boundaries, generating highly mobile electrons and lattice vibrations (phonons), as compared with the nanoparticles produced during RCE method. These radiations seem also to shoot the smaller nanoparticles from internal pore system to outer surface in more organized style, specifically for the higher Pt loading (viz., 0.9 wt %). These actions reflect thereby on the electrical properties and catalytic performances in several petrochemical processes.

3.3. Catalytic performances of various Pt/SiO2 nanocatalyst samples

3.3.1. In ethanol conversion

Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36

The catalytic activity parameters of Pt/ SiO₂ nanocatalyst samples (of 0.3 wt %, 0.6 wt % and 0.9 wt % Pt loadings), synthesized via MAS or RCE reduction method, were investigated in ethanol conversion, in the temperature range $250-450^{\circ}$ C, as illustrated in Fig. 8. All catalyst samples under study exhibited the main activity toward production of ethylene, i.e., toward dehydration pathway of the reaction, with much lower activity toward acetaldehyde production (dehydrogenation pathway). The % conversion of ethanol increased markedly with rising the reaction temperature and decreased slightly with the Pt loading. This seemed to be related to the dispersion behavior of supported Pt nanoparticles [21]. However, the selectivity toward ethylene, achieved at 450° C for the 0.6 wt % and 0.9 wt % Pt loaded samples synthesized via MAS method, was somewhat higher (viz. 50-53 %) than those values obtained for the samples prepared by RCE method (~47 %). For the diluted catalyst sample (of 0.3 wt % Pt) prepared by RCE method, the ethylene yield % (27%) and selectivity to ethylene (53%) at 450° C were higher than those values noticed for the samples prepared via MAS method (23% and 50%, respectively). These findings run in harmony with the dispersion parameters of Pt NPs, highlighting the role of nanosilica support in this reaction. On the other hand, the produced acetaldehyde, detected only in low yields in this reaction, was found to increase with temperature and with % loading of Pt nanoparticles, achieving its maximum yield at 400° C for the 0.9 wt % loaded sample prepared by RCE method (22 % vs. 19 % for the corresponding sample synthesized via MAS method).

3.3.2. In cyclohexane conversion

The same catalyst samples under study were examined in cyclohexane conversion in the temperature range, 300° C – 450° C, the results of which are represented in Fig. 9. It is evident that all samples of different loadings, synthesized by both MAS and RCE reduction methods, display the main activity toward dehydrogenation pathway of the reaction, achieving almost 100 % selectivity to benzene all over the temperature range in all cases [22, 23]. Virtually, no activity for the undesired hydrogenolysis pathway, producing light hydrocarbons of low value could be observed. This may be acknowledged to the probable maximized hydrogen spillover effect under the applied experimental conditions. The % conversion of cyclohexane as well as the benzene yield (%) increased gradually with rising the reaction temperature and with the Pt loading, especially from 0.3 % to 0.6 % Pt content prepared by both reduction procedures [22-24].

This could be referred to the dispersion behavior of the optimized nanostructure of supported Pt particles; related mostly to the interaction profile of Pt species with surface hydroxyls of nanosilica support. These two activity parameters are clearly higher for the samples prepared by RCE method, characterized by preservation of major fraction of Pt nanoparticles in silica pore system. However, the 0.9 wt % Pt loaded sample prepared by MAS method could be

RSC Advances

distinguished as exhibiting some hydroisomerization activity to methylcyclopentane (mcp), at the expense of benzene production. This may be interpreted in view of the suggestion that MAS procedure could shoot a fraction of supported Pt NPs outside the pore system, as mobile surface species that seemed to expose some hydroxyl groups, presumably Brønsted acid sites, to function in producing mcp. In contrast, the identical sample prepared by RCE method, of deeply incorporated fraction of Pt NPs, showed the same activity pattern as in the remaining samples.

Table 4: TOF for ethanol and cyclohexane conversions on different Pt/SiO₂ catalyst samples synthesized through MAS or RCE reduction methods

Catalyst	TOF (benzene)	TOF (ethylene)			
	$(10^{-3} \mathrm{s}^{-1})$	$(10^{-3} \mathrm{s}^{-1})$			
Samples synthesized by MAS method					
0.3 Pt-Si	11.9	13.2			
0.6 Pt-Si	10.7	9.6			
0.9 Pt-Si	7.1	5.3			
Sampl	es synthesized by RC	E method			
0.3 Pt-Si	17.2	11.1			
0.6 Pt-Si	20.6	11.8			
0.9 Pt-Si	21.8	19.3			

The turnover frequencies (TOF) were calculated using the Pt loading, measured reaction rate (ethanol and cyclohexane conversions) at the end of the reaction at 400° C and the number of exposed Pt atoms on the sample surface estimated from the degree of dispersion (Table 2) related directly to the average size of Pt NPs. The results summarized in Table 4 indicate that TOFs of the reactions to selectively produce ethylene (from ethanol) or benzene (from cyclohexane) on the catalyst samples synthesized by MAS reduction decreases with Pt loading, i.e., with the number of exposed Pt atoms, especially on the surface of the 0.9 Pt-Si sample, where MAS irradiation encouraged the transfer of smaller Pt NPs from wider fraction of mesopores to the outer top surface. The dispersed nanoparticles (3-7 nm, Table 2) seem to be responsible of the activity in both reactions tending probably to be structure insensitive. On the other hand, the samples reduced by RCE method exhibit increasing TOF values with Pt loading (in agreement with the total conversion data). The decreased number of exposed atoms related to the enlarged average sizes of the surface Pt NPs (reaching to 15.5 nm, Table 2) seems to control the reactions in these cases, being most probably structure sensitive.



Fig.8: Catalytic Activity of Pt/ SiO_2 nanocatalyst samples of 0.3, 0.6 and 0.9 wt % Pt loadings synthesized via MAS reduction method (A, B, C) and by RCE method (C, D, F) in ethanol conversion.



Fig.9: Catalytic Activity of Pt/ SiO₂ nanocatalyst samples of 0.3 wt %, 0.6 wt % and 0.9 wt % Pt loadings synthesized via MAS reduction method (A, B, C) and by RCE method (C, D, F) in cyclohexane conversion.

4. Conclusion

Silica nanopowder used in this study seemed to have high surface area and consisted of fine, homogenous and well distributed nanoparticles of an average size ≤ 2 nm. The SiO₂supported Pt nanocatalysts (of 0.3, 0.6 and 0.9 wt % loadings) were synthesized via microwave-assisted solution (MAS) method or rotary chemical evaporation (RCE) method in the in situ reduction step. The samples synthesized via MAS method exhibited higher surface areas, with decreased pore dimensions, especially for diluted samples, compared with those samples synthesized by RCE method. With increasing the metal loading, probably a transfer of some of Pt NPs out of the pore system to top silica surface by MAS effect was suggested. The MAS reduction method achieved also more organized distribution of less sized Pt NPs, not exceeding 10 nm, on silica surface, compared with the RCE method, resulting in uneven distribution of larger Pt NPs (\geq 33 nm). The results of AC conductivity and dielectric constants confirmed that the electromagnetic radiations in MAS method enhance the even distribution of smaller in size Pt NPs with higher concentration of grain boundaries, generating highly mobile electrons and lattice vibrations (phonons), as compared with nanoparticles produced during RCE method. The radiations encouraged shooting the smaller NPs from the inner pore system to the outer surface in more organized style, in the higher

metal loaded samples (viz., 0.9 wt % Pt). TOFs of the reactions to selectively produce ethylene (from ethanol) or benzene (from cyclohexane) decreased with Pt loading on catalyst samples synthesized by MAS method, i.e., with the increase in number of exposed surface Pt atoms. The dispersed NPs (of 3-7 nm) seemed to be responsible of the activity in both reactions, tending to be structure insensitive. However, the samples reduced by RCE method exhibited increasing TOF values with Pt loading. The decreased number of exposed atoms related to the enlarged average sizes of the surface Pt NPs (approaching 15.5 nm) seemed to control the reactions in these cases, tending most probably to be structure sensitive.

References

Published on 09 June 2015. Downloaded by University of Manitoba on 10/06/2015 12:32:36

- [1] Li, Z. X.; Shi, F. B.; Li, L. L.; Zhang, T.; Yan, C. H. Phys. Chem. Chem. Phys. 2011, 13, 2488-2491.
- [2] Ogino, I.; Chen, C. Y.; Gates, B. C. Dalton Trans. 2010, 39, 8423-8431.
- [3]Mingshu, C.; Wayne, G. D. Chem. Soc. Rev. 2008, 37, 1860-1870.
- [4] R. L. Jia, C. Y. Wang, S. M. J. Wang, Mater. Sci. 41 (2006) 6881-6888.
- [5] Min, B. K.; Santra, A. K.; Goodman, D. W. Catal. Today 2003, 85, 113-124.
- [6] Moon, D. S.; Lee, J. K. Langmuir 2012, 28, 12341-12347.
- [7] Dutta, P.; Sarkara, A. Adv. Synth. Catal. 2011, 353, 2814 2822.
- [8] Haifeng, Y.; Qingyi, L.; Feng, G.; Qihui, S.; Yan, Y.; Fuqiang, Z.; Songhai, X.; Bo, T.; Dongyuan, Z. Advanced Functional Materials. 2005, 15(8), 1377-1384.
- [9] Peiyu, W.; Qingshan, L.; Jiangong, L. Materials Research Bulletin. 2010, 45, 129-134.
- [10] White, R. J.; Luque, R.; Budarin, V. L.; Clark, J. H.; Macquarrie, D. J. Chem. Soc. Rev. 2009, 38, 481-494.
- [11] Neelgund, G. M.; Aderemi, O. Applied Catalysis, A: General. 2011, 399(1-2), 154-160.
- [12] Farrukh, M. A.; Heng, B. T.; Adnan, R. Turk. J. Chem. 2010, 34, 537-550.
- [13] A. Bayrakçeken, L.Türker, I.Eroğlu, Improvement of carbon dioxide tolerance of PEMFC electrocatalyst by using microwave irradiation technique. "Int. J. of Hydrogen Energy", 33, (2008), p.7527-7537.
- [14] J.P. Tierney and P. Lidstrom, Microwave Assisted Organic Synthesis; CRC Press: Boca Raton, FL, USA, 2005.
- [15] M.M. Gomaa, H.M. Gobara, Electrical properties of Ni/silica gel and Pt/γ-alumina catalysts in relation to metal content in the frequency domain, Materials Chemistry and Physics 02/2009; 113(s 2–3):790–796.
- [16] H. M. Gobara and M. M. Gomaa, II. Electrical Properties of Ni/Silica Gel and Pt/-Alumina Catalysts in Relation to Catalytic Activity, Petroleum Science and Technology, 27:1572–1591, 2009.
- [17] Chaudhari, S.C.; Patil, R. N. Advances in Applied Science Research, 2012, 3 (6):3848-3854.
- [18] Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquerol, Pure and Applied Chemistry, 57 (1985) 603.
- [19] H. M. Gobara, S. A. Hassan, A Comparative Study of Surface Characteristics of Nickel Supported on Silica Gel, γ-Alumina, Aluminosilicate, Petroleum Science and Technology, (2009)27(14):1555-1571.
- [20] Gomaa M. M., 2009, Saturation effect on electrical properties of hematitic sandstone in the audio frequency range using non-polarizing electrodes, Geophysical Prospecting, Vol. 57, pp. 1091–1100.
- [21] H.M. Gobara, R.S. Mohamed, F.H. Khalil, M.S. El-Shall, S.A. Hassan, Various characteristics of Ni and Pt–Al₂O₃ nanocatalysts prepared by microwave method to be applied in some petrochemical processes, Egyptian Journal of Petroleum (2014) 23, 105– 118.
- [22] Osama Saber, Heba M. Gobara, Current Nanoscience, 9 (2013) 394-400.

[23] Osama Saber, Heba M. Gobara, Current Nanoscience, 9 (2013) 654-661.
[24] O. Saber, H.M. Gobara, A.A. Al Jaafari, Appl. Clay Sci. 53 483 (2011) 317–325.