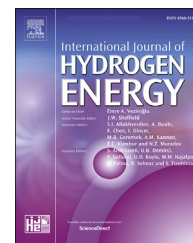


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On the role of size controlled Pt particles in nanostructured Pt-containing Al₂O₃ catalysts for partial oxidation of methane



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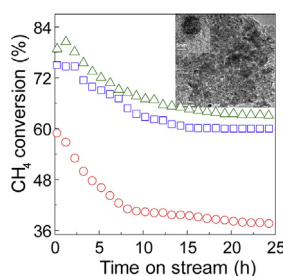
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HIGHLIGHTS

- Partial oxidation of methane reaction over nanostructured Pt supported Al₂O₃.
- XRD, Nitrogen-sorption, H₂-TPR, CO-DRIFTS, SEM-EDS, XPS and HRTEM.
- The metal dispersion evaluated in the cyclohexane dehydrogenation reaction.
- The effect of the Pt particles sizes and loadings on the stability of catalysts.
- Enrichment of Pt⁰ nanoparticles on the surface avoids heavy carbon deposition.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of the Pt loadings and particles sizes on the stability of Pt(x wt%)/Al₂O₃ catalysts were investigated in the partial oxidation of methane (POM) reaction. The Al₂O₃ support was prepared by sol-gel method and different Pt loadings, varying from 0.5 to 2.0 wt% were incorporated to alumina through the incipient wetness impregnation method. The physicochemical features of the catalysts were determined by XRD, ICP-OES, Nitrogen-sorption,

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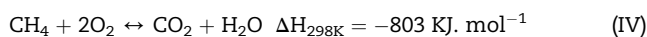
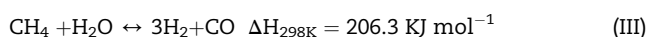
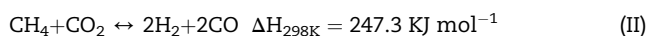
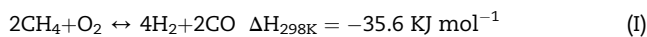
UV–Visible, H₂-TPR, CO-DRIFTS, SEM-EDS, XPS and HRTEM techniques. The metal dispersion was evaluated in the cyclohexane dehydrogenation reaction. Lower Pt loadings resulted in well dispersed Pt⁰ nanoparticles with an enhanced activity in cyclohexane dehydrogenation and POM reactions. With increasing Pt loading to 2.0 wt%, the Pt nanoparticles of the Pt(2.0 wt%)/Al₂O₃ showed a methane conversion of 63% in 24 h of time on stream, and the catalyst was very selective to H₂ and CO. Based on the HRTEM, XPS and Raman spectroscopy techniques, an increment in the Pt loadings evidenced an enrichment of Pt⁰ clusters on the surface, however, no heavy carbon deposits formation was observed.

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Introduction

Catalytic partial oxidation of methane (POM) has emerged, in the last few decades, as a technologically interesting alternative for natural gas utilization [1–3]. Through POM, methane is converted into synthesis gas (H₂ and CO), which is a versatile and economically attractive route due to the further syngas transformation into valuable chemicals intermediates such as methanol and dimethyl ether [3–5].

Compared to the other syngas processes, the POM reaction (I) is advantageous over dry reforming (II) and steam reforming reactions (III), owing to its mild exothermicity and synthesis gas production with a ratio of 2 [2,4–6]. Also, both POM (I) and total combustion of methane (IV) reactions offer the possibility of operating at high space velocities of (1.0–5.0) × 10⁵ h^{−1} [4]. Indeed, the aforesaid H₂/CO ratio is a suitable condition to be directly used for Fisher–Tropsch synthesis and methanol production [1,2,7]. Regarding the safety, a high CH₄/O₂ ratio and low pressures are also desired to avoid danger of explosions for practical POM applications [7,8].



There is currently a wide selection of supported transition metal-based catalysts, including Pt, Co, Ru, Fe, Ir, Pd, Ni and Rh ones, which are found to be active and stable for POM [2–12]. Among them, the noble metals catalysts are considered relatively selective and stable than the non-noble counterparts. Because POM is classified as structure sensitive reaction, the cleavage of the C–H bond from CH₄ molecule occurs predominantly on the edge and corner of the metal atoms [2]. Although most studies claim that the catalysts are stable in POM, the decline of their conversions may be caused by the decrease in the noble metal dispersion on support surface, sintering of the Pt particles, phase transformation of the support and coke formation, as reported elsewhere [2,8–11].

Based on these facts, the support plays an important role in POM and most studies have focused on perovskites, molecular

sieves, spinel oxides, alumina, zeolites, single oxides, hydro-talcites, carbides and silica supports, among which alumina is highly effective for POM and other catalytic hydrocarbons transformation [7–13]. In this context, several studies has also been devoted to the development of alumina supported noble metal catalysts in POM, each of them showing their own metal-support characteristics [2–4,9,12].

Attempts to minimize the alumina support phase transformation (e.g., $\gamma \rightarrow \alpha$) have been made to avoiding its deterioration and simultaneously, it may contribute to circumvent the metallic phase sintering [1–4,9]. Our previous reports on the Pt/Al₂O₃ have shown that the preparation method of the support resulted in a robust catalyst to retard coke formation and methane decomposition reactions during steam and dry reforming of methane [14–16].

The reported preparation procedures allow for a broad distribution of active Pt species particle sizes [14,16]. Although a large number of other supported Al₂O₃ redox catalysts for methane transformations, including those with Rh, Pd, Ni, Pt and Ru are also found to be active and selective in POM, new insights on the effect of the Pt loadings and particles sizes on Al₂O₃-supported ones to obtain a coke resistance catalyst are lacking. Therefore, a clear comprehension of the structure-activity relationships for Pt size effects and the influence of Pt dispersion in the C–H bond cleavage during CH₄ activation in POM are often lacking.

In this work, the effect of the Pt loadings on the activity and selectivity of the nanostructured Pt/Al₂O₃ catalysts was investigated in POM reaction. This study gives approaches for the detailed particle sizes influences on POM over the nanostructured supported catalysts. To the best of our knowledge, there are no works that report on the Pt loadings over the nanostructured supported Pt/Al₂O₃ catalysts in POM reaction.

Experimental

Catalyst preparation

The catalysts were synthesized according to the sol–gel method, as described in our previous study [14,15]. Briefly, Al₂O₃ xerogel was prepared and calcined at 950 °C. The wetness impregnation of the platinum on the calcined Al₂O₃ support was through the use of the ethanolic solution of

$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Degussa). About 0.5 wt% of Pt was impregnated in 1 g of the Al_2O_3 support, and after removing the excess of ethanol in a rotatory evaporator, the solid was thoroughly washed with water, dried and calcined at 350 °C under synthetic air flow. The solid was designed as Pt(0.5 wt%)/ Al_2O_3 . The platinum loadings were varied in 1.0 and 2.0 wt%, being the samples were labeled as Pt(1.0 wt%)/ Al_2O_3 and Pt(2.0 wt%)/ Al_2O_3 , respectively. These prepared solids are generally designed as Pt(x wt%)/ Al_2O_3 .

Characterization

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku Multiflex diffractometer using Cu K α source. The diffractograms were obtained in the 2θ region of 5–80° with a 0.02 step-scan (step time = 2s). All patterns were obtained and compared with those of the Joint Powder Diffraction Committee files (JCPDS).

The Pt loadings were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) chemical analysis. The experiments were carried out using a AtomScan 25 spectrometer (Thermo Jarrel Ash). Prior to the experiments, the solids were digested in nitric acid and heated in a sand bath and then, the residual solid was diluted in a HNO_3 solution.

Nitrogen physisorption experiments were performed through the isotherms at –196 °C using a Micromeritics ASAP 2000 equipment. Prior to the analyses, the samples were degassed under vacuum at 200 °C for 2 h. The specific area, average pore size and total pore volume of catalysts were determined by the BET and BJH methods, respectively.

UV–vis diffuse reflectance spectra (DRS) were recorded in a Cary 5G UV–Vis–Nir Varian spectrometer, which was equipped with an integrating sphere. The spectra were obtained between 200 and 800 nm.

Temperature-programmed reduction experiments (H_2 -TPR) were carried out in Micromeritics Pulse Chemisorb 2705 equipment coupled with a thermo conductivity detector (TCD). Before measurements, about 0.1 g of the sample was pretreated at 150 °C with nitrogen as a carrier for 1 h. After the temperature was reduced to 25 °C, the H_2 -TPR experiments were carried out by heating temperature up to 1000 °C with a ramping rate of 10 °C min^{-1} using 5% H_2/Ar (50 mL min^{-1}) as reduction gas. Also, a cold trap filled with a mixture of propanol–liquid nitrogen was used to remove water formed during the reduction, before the TCD analyses.

The CO adsorption measurements were followed by Fourier Transformed Infrared using a Thermo Nicolet 4700 Nexus FT-IR spectrophotometer with MCT detector and Diffuse Reflectance Infrared Fourier Transform Spectroscopy- DRIFTS reactor cell (Spectra Tech). The equipment was connected to a gas-dosing evacuation system and it was equipped with the CaF_2 windows (DRIFT HTHV cell). The (CO- DRIFTS) spectra were recorded with at 4 cm^{-1} resolution using 64 scans. Before the measurements, the catalysts were reduced at 650 °C under a 25% H_2/N_2 flow for 2 h. The adsorption of CO was carried out at 25 °C with CO pulses (0.5 mL min^{-1}) at a CO pressure of 20 Torr. More experimental details on CO-FTIR measurements were provided in ref. [15].

High-Resolution Transmission Electron Microscopy (HTEM) imaging was performed on a JEOL JEM-3010 microscope at an operating voltage of 300 kV and 1.7 Å point

resolution. For selected reduced and spent solids, the TEM images were collected using a Jeol JEM 2100 microscope. Previously, the samples were prepared by mounting an isopropanol-dispersed sample on a lacey carbon films supported on copper grids.

The morphologies and elemental composition were studied by scanning electron microscopy (SEM), using a JEOL 2000 FX microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) detector with the acceleration voltage of 20 kV. Previously, the selected reduced and spent catalysts were deposited on an aluminum sample holder and then sputtered with gold to perform the analyses.

X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB 200R spectrometer equipped with a hemispherical electron analyzer and Al K α source ($h\nu = 1486.6$ eV, $1 \text{ eV} = 1.6302 \times 10^{19}$ J). Binding energies (± 0.2 eV) were determined with respect to the C 1s line at 284.8 eV. The spectra of the O 1s, Al 2p, C 1s and Pt 4d regions were measured. The fittings were in a XPSpeak1 software whereas the curves produced were determined with different proportions of Lorentzian and Gaussian functions. The $I_{\text{Pt}}/I_{\text{Al}}$ intensity and C/Al surface ratios were obtained using the area of the peaks corresponding to Al 2p, Pt 3d and C 1s core levels. Raman spectroscopy measurements were performed for the spent solids. The Raman spectra were measured using a LabRam spectrometer equipped with a charge coupled device. The excitation source line was 532 nm with the laser power of 20 mW.

Catalytic tests

Partial oxidation of methane (POM)

The catalytic performances of the solids were evaluated in the partial oxidation of methane using a fixed-bed down flow reactor at atmospheric pressure. Typically, 40 mg of the sample was mixed with the diluent (SiC) and then, placed in between two quartz wool plugs in the center of the quartz tube reactor. Previously, the sample was heated at 150 °C under nitrogen flow with a rate of 30 mL min^{-1} for 0.5 h. Thereafter, the sample was reduced at 650 °C under hydrogen flow at 30 mL min^{-1} for 2 h. After activation, the sample was heated to 800 °C using nitrogen as carrier. The $\text{CH}_4/\text{O}_2/\text{N}_2$ molar ratio of 2:1:0.9 was used. The reaction was carried out with the pre-treated samples and the aforesaid gas mixture was fed through the reactor at 130 mL min^{-1} . The reaction products were analyzed using online gas chromatography (Varian 3800) using with a Chrompack CP-Wax 57 CB column capillary column coupled to a FID detector.

Dehydrogenation of cyclohexane to benzene reaction

The Pt dispersion was evaluated through the dehydrogenation of cyclohexane reaction, an insensitive structure reaction [14]. About 10 mg of the catalyst powders were loaded into the fixed-bed reactor at atmospheric pressure. The catalysts were pre-reduced in the H_2 flow (30 mL min^{-1}) at 650 °C for 2 h, before the dehydrogenation of cyclohexane reaction. The reaction was carried out at 170 °C with a WHSV of 170 h^{-1} . The cyclohexane was fed to the reaction by bubbling hydrogen through a saturator containing the liquid hydrocarbon at 12 °C. The outlet gases were analyzed, after water condensation, with a HPIN-NOWAX capillary column in the HP5890 gas chromatography.

Results and discussion

XRD and DRS measurements

XRD patterns of all Pt (x wt%)/Al₂O₃ catalysts display broad features typical of semi-crystalline solids (Fig. 1). Some reflections arising from cubic γ -Al₂O₃ with *Fd*-3*m* space group (JCPDS 10–425) appear in the XRD patterns of the solids. These reflections arise concomitantly with those of monoclinic θ -Al₂O₃ (C2/*m* space group; JCPDS 11–0517) as observed for the pure Al₂O₃ sample. No differences in terms of crystallinity are seen, when comparing solids with different Pt loadings (Fig. 1). It is reasonable to believe that the distinct Pt loadings as well as small Pt particle sizes will not affect the dispersion on the carriers, as later observed by other characterizations techniques.

The DRS bands for the Pt(x wt%)/Al₂O₃ catalysts (Fig. 2) depicts two intense charge-transfer bands coming from the O atom from the support or chloride ions to Pt at 224 nm with a shoulder at 260 nm, as in case of Pt(0.5 wt%)/Al₂O₃ [18]. This is in agreement with the bands coming from hexachloroplatinic acid in solution showing charge-transfer bands at around 202 and 266 nm [17]. The second band is due to the d-d transitions of Pt at 330 nm, in agreement with the findings [17,18]. Comparing the solids with different loadings of Pt, the bands of Pt(1.0 wt%)/Al₂O₃ become more intense and broader with the concomitant evidence of the shoulder at around 256 nm, as well. Moreover, the displacement of the bands the d-d transitions to low wavenumber regions as in case of Pt(2.0 wt%)/Al₂O₃ correspond to the increase in the metallic charge with the consequent weakness of the metal-support interaction between [Pt^{IV}(OH)_xCl_y] or yet, (PtO_xCl_y)_s type species and the Al₂O₃ support surface. These facts agree with those of the findings [17]. As found elsewhere, the presence of OH groups on the support surface favors the strong interaction of the carrier with the Pt species [19]; however, the amount of OH surface species in the samples studied is probably the same as the solids are calcined at 300 °C.

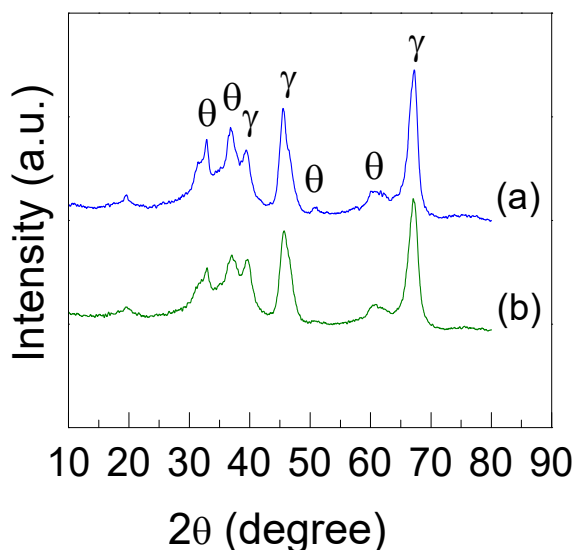


Fig. 1 – XRD patterns of the Pt(x wt%)/Al₂O₃ catalysts: (a) Pt(1.0 wt%)/Al₂O₃ and (b) Pt(2.0 wt%)/Al₂O₃.

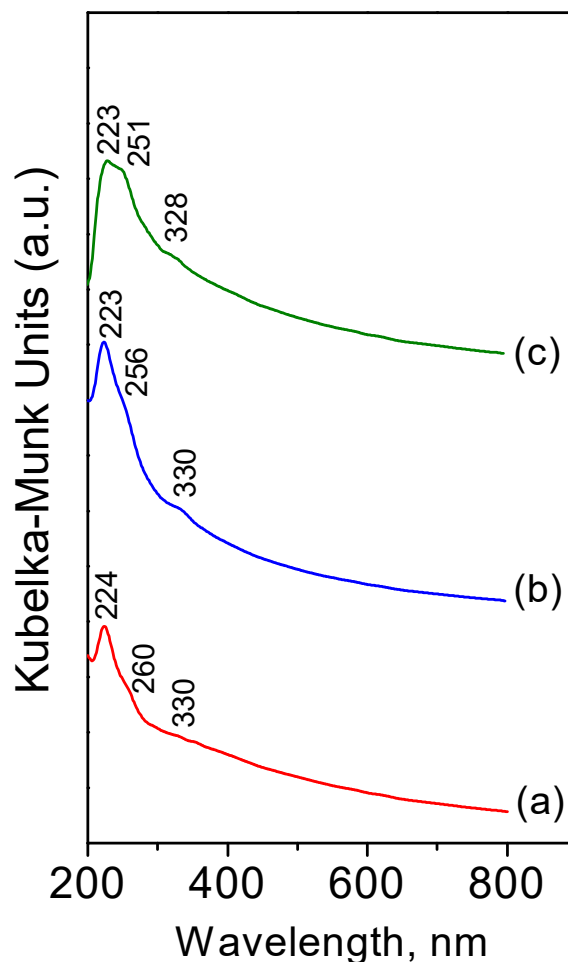


Fig. 2 – DRS spectra of oxidized catalysts: (a) Pt(0.5 wt%)/Al₂O₃, (b) Pt(1.0 wt%)/Al₂O₃ and (c) Pt(2.0 wt%)/Al₂O₃.

Furthermore, the presence of PtO₂ species along with big PtO particles facilitates the increase of the d-d transitions band ([17,18] and references herewith). This results in a weakening of the Pt–O and Pt–Cl bonds in the support surface and lessening of the energy levels separation in the catalyst. Similar effects can be inferred for Pt(2.0 wt%)/Al₂O₃ catalyst most probably due to a Pt particle size increase, as latter observed by TEM.

Important is to say that the UV–Vis bands of Pt(0.5 wt%)/Al₂O₃ and Pt(1.0 wt%)/Al₂O₃ are narrow compared with Pt(2.0 wt%)/Al₂O₃, which indicates that the low metal-support interactions are likely at high Pt loadings.

Textural properties and morphological examinations of the solids

The textural properties of the catalysts are obtained through physisorption of N₂ (Table 1).

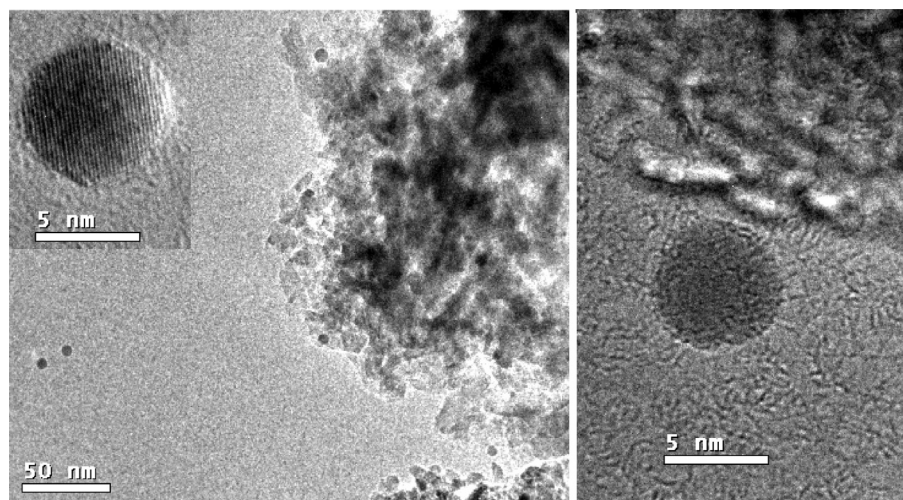
All solids have type IV isotherms (not shown), which is typical of mesoporous materials. The BET surface areas are estimated by the nitrogen adsorption-desorption isotherms.

An increment in the Pt loadings results in the decreasing trend in the textural properties of the Pt(x wt%)/Al₂O₃ catalysts. For instance, the Pt(0.5 wt%)/Al₂O₃ has a BET surface

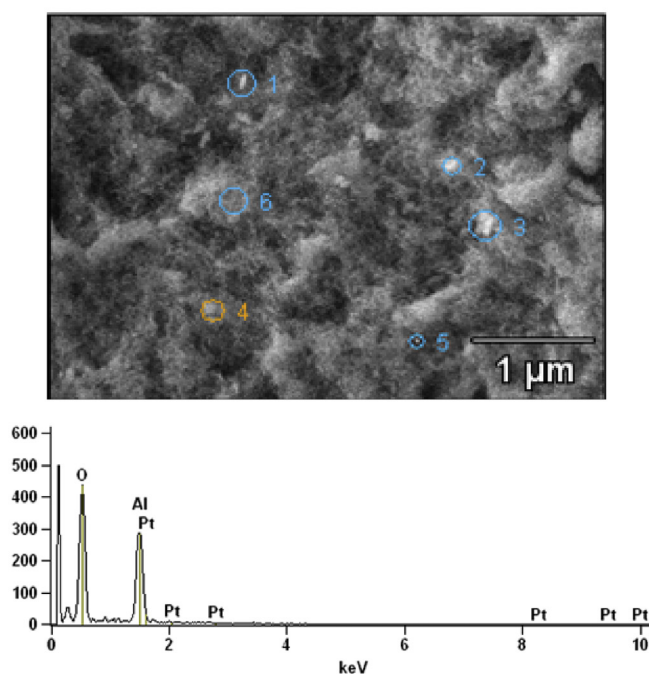
Catalysts	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_p ($\text{cm}^3 \cdot \text{g}^{-1}$)	D_p (nm)	Cyclohexane dehydrogenation ^a		E_{app} ($\text{kJ} \cdot \text{mol}^{-1}$)	SRM ^b	r_d	POM ^c
				D_{ptt} (%)	$r_d \cdot 10^{-5}$ ($\text{mol} \cdot \text{s}^{-1} \cdot \text{gcat}^{-1}$)				
Pt(0.5 wt%)/Al ₂ O ₃	215	0.25	8.1	76	7.13	76.4	5.52	1.3	34.6
Pt(1.0 wt%)/Al ₂ O ₃	118	0.24	8.2	53	5.01	71.8	4.52	1.1	31.8
Pt(2.0 wt%)/Al ₂ O ₃	129	0.27	8.3	—	1.83	70.4	8.40	0.2	—

^a Rate of cyclohexane dehydrogenation at 270 °C.
^b Rate and Turnover frequency of steam reforming methane at 500 °C.
^c Turnover frequency (TOF) of partial oxidation of methane at 800 °C and 0.5 h.

As the Pt loading is increased, the reduction peaks of Pt(1.0 wt%)/Al₂O₃ notably shifts to low temperatures, indicating that a low metal-support interaction is occurring, and thereby make the Pt species easier to be reduced. This is due to the Pt



(a)



(b)

Fig. 3 – TEM image of the reduced selected samples: (a) TEM image of Pt(0.5 wt%)/Al₂O₃ and (b) The representative EDS spectra and SEM image of Pt(2.0 wt%)/Al₂O₃ and the TEM images are also shown.

species with slight big sizes giving a lesser intimate Pt–Al interaction. When the Pt loading is of ca. 2.0 wt% as in Pt(2.0 wt%)/Al₂O₃, the temperatures of reduction notably lower and the peaks change their intensities comparing with the samples with low Pt loadings. This implies in the formation of large amounts of clusters of [Pt^{IV}(OH)₄Cl₂]_s species on the support, which consumes more hydrogen at around 207 °C for Pt(2.0 wt%)/Al₂O₃. Simultaneously, a strong interaction of the [Pt^{IV}O_xCl_y]_s seems to occur at 2.0 wt% of Pt for the second peak with a shoulder at around 451 °C.

The CO-DRIFTS measurements are further adopted to verify the nature and accessibility of Pt particles and their

interactions with CO in the samples. On Pt (x wt%)/Al₂O₃ catalysts (Fig. 5), it is possible to observe the presence of one band in the region of 2063 cm^{−1}, which is ascribed to the presence of CO linearly bonded to one Pt atom, as found with Pt loading of 0.5 wt% in ref. [15]. The further component would be a shoulder at 2076 cm^{−1}, being attributed to linear CO species adsorbed on terrace Pt atoms interacting with the hydroxyl surface of alumina [14,19]. Of those bands, the latter appears in the same frequency as that at about 2081 cm^{−1}, which is typical of Pt⁰(CO) from high reducibility of Pt oxide by CO [19].

An increase in the Pt loadings from 0.5 to 2.0 wt% gives a steady displacement of the bands to high frequencies regions.

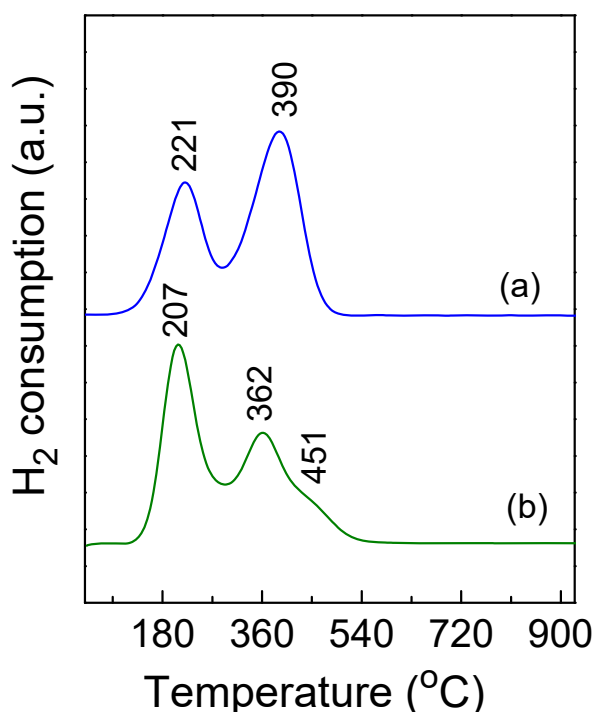


Fig. 4 – TPR curves of the fresh Pt(x wt%)/Al₂O₃ catalysts: (a) Pt(1.0 wt%)/Al₂O₃ and (b) Pt(2.0 wt%)/Al₂O₃.

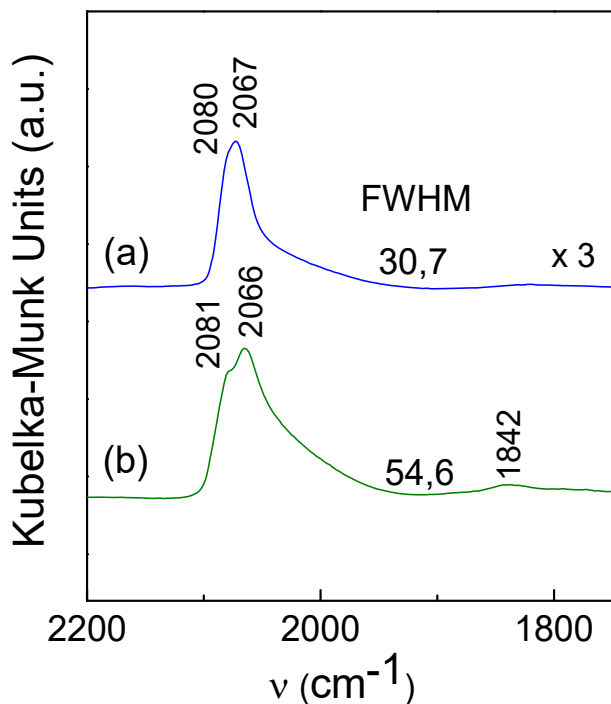


Fig. 5 – DRIFTS spectra of adsorbed CO on reduced catalysts: (a) Pt(1.0 wt%)/Al₂O₃ and (b) Pt(2.0 wt%)/Al₂O₃.

Moreover, a band appearing at 1842 cm⁻¹ at low frequencies regions in Pt(2.0 wt%)/Al₂O₃ indicates that the CO is bonded to two surface Pt atoms, giving proof that bridged Pt species are formed [17,21]. Also, it could indicate that CO is adsorbed on

small Pt particles possessing high electron densities [15]. Furthermore, the intensity increases with the consequent drop in the full width at half-maximum (FWHM) from 40.1 to 30.7, respectively for 0.5 and 1.0 wt% of Pt [15]; suddenly, the intensity of the bands increase in reason of the greater adsorption of CO with more Pt atoms [18]. Indeed, the FWHM (e.g. 54.6) also increases due to the heterogeneity of Pt particles possessing distinct electronic density on solid surface.

Surface and electronic properties

XPS of the fresh and reduced catalysts are further used to describe the electronic effect of Pt on the supports. The binding energies (BE) of O 1s, Al 2p and Pt 4d_{5/2} core electrons and the surface atomic ratios are listed in Table 2.

In all cases of the fresh Pt(x wt%)/Al₂O₃ catalysts, the binding energies of O 1s are 531.4 eV, which is associated with the bulk oxygen species (Al–O–Al) from the γ-Al₂O₃ and θ-Al₂O₃ phases support (XRD results). No difference in the BE peak positions is noted for O 1s contributions, when the Pt(x wt%)/Al₂O₃ solids are reduced, confirming the stability of the support. With regards to the Al 2p species, the Al³⁺ species contributions are within the BE from 74.1 to 74.6 eV for both oxidized or reduced, independently of the Pt loadings. There is some consensus in the literature that the BE of Al 2p for Al₂O₃ is 74.1 eV with variations between 0.2 and 0.5 eV [20], which confirms our results.

Moreover, analysis of the Pt 4d_{5/2} core levels shows that the fresh samples have BE of 315.0 ± 0.6 eV. According to the literature, the presence of Pt²⁺ and Pt⁴⁺ is observed for BE of 315.3 and 317.0 eV, respectively [20]. Based on these facts, the Pt oxidized species found in this study for fresh catalysts can be correspondingly described as of Pt²⁺ and Pt⁴⁺, which is in line with the results of DRS and CO-DRIFTS.

Compared to the reduced samples, the BE for have a significant change from 314.0 to 313.9 eV, indicating the characteristic feature of metallic Pt is predominantly found on the solids. Also, an increase in the Pt/Al concentrations (measured by the I_{Pt}/I_{Al} ratio, Table 2) with raising Pt loadings for more than 0.5 wt% is observed, when the solids are reduced. Similar trends are observed for the fresh ones. This demonstrates that a higher coverage of both reduced and fresh Pt species on the support surface may occur at Pt loadings >0.5 wt%.

Table 2 – XPS parameters of oxidized and reduced Pt(x wt%)/Al₂O₃ catalysts.

Catalysts		BE (eV)			Intensity ratio (×10 ⁻²) I _{Pt} /I _{Al}
		O 1s	Al 2p	Pt 4d _{5/2}	
Pt(0.5 wt%)/Al ₂ O ₃	Oxid.	531.4	74.2	315.1	3.97
	Red.	531.3	74.1	314.0	1.62
Pt(1.0 wt%)/Al ₂ O ₃	Oxid.	531.5	74.6	315.6	5.50
	Red.	531.3	74.5	313.9	3.62
Pt(2.0 wt%)/Al ₂ O ₃	Oxid.	531.3	74.6	315.5	10.03
	Red.	531.1	74.5	314.0	6.58

Samples treated in air at 350 °C and reduced catalyst at 650 °C.

Cyclohexane dehydrogenation to benzene reaction

The catalytic performance of various catalysts for cyclohexane dehydrogenation is investigated with the aim of showing the Pt particles dispersion on the supports. The catalytic results are expressed by the rate of cyclohexane dehydrogenation (Table 1). As the title reaction is insensitive to structure, the cyclohexane is found to dehydrogenate on Pt sites with rates varying directly according to the density of available Pt sites for the reaction at the temperature of reaction [15,16].

Within the Pt(x wt%)/Al₂O₃ catalysts, the cyclohexane readily is chemisorbed over the Pt sites and then

dehydrogenates depending on the capacity of the metal to coordinate not a hydrogen atom but a “hydride.” [21]. The cyclohexane dehydrogenation rate (r_d) of the catalyst possessing 0.5 wt% of Pt is found to be $7.13 \times 10^{-5} \text{ mol. s}^{-1} \text{ gcat}^{-1}$ with the corresponding 76% of Pt dispersion. Any possible well dispersion of Pt particles leads to smaller active particle formation on the alumina surface for cyclohexane dehydrogenation to benzene reaction.

For comparisons purposes, the catalytic performance of Pt(0.5 wt%)/Al₂O₃ in SRM reaction as r_{SRM} , E_{app} and TOF are $5.52 \text{ mol s}^{-1} \text{ gcat}^{-1}$, 76.4 kJ mol^{-1} and 2.7 s^{-1} , respectively (Table 1). This results in a rate between cyclohexane dehydrogenation

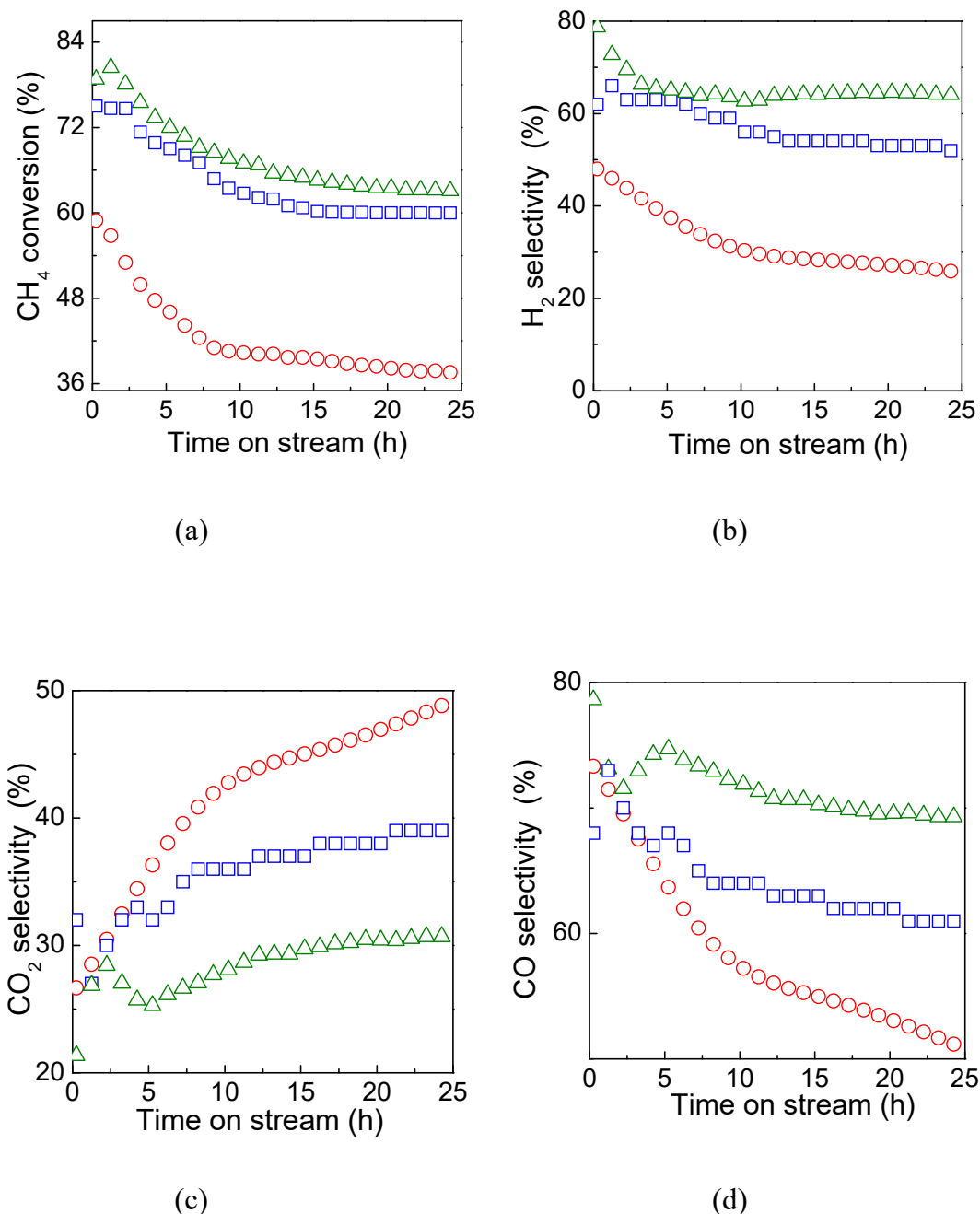


Fig. 6 – Catalytic evaluation of the solids in the partial oxidation of CH₄ reaction at 800 °C for 24 h of time on stream. (a) Methane conversion and (b) Hydrogen, (c) carbon monoxide and (d) carbon dioxides selectivities are taking with the following samples: (○) Pt(0.5 wt%)/Al₂O₃, (□) Pt(1.0 wt%)/Al₂O₃, and (△) Pt(2.0 wt%)/Al₂O₃.

and steam reforming (r_d/r_{SRM}) of 1.3. These values are in good agreement with those previously reported for Pt, Rh, Ir supported on alumina and zirconia catalyst, in steam reforming of methane that suggest the highest metal dispersion giving the highest number of converted CH_4 molecules for SRM, [15]. This is an indication that the well dispersed Pt samples are ready to convert methane and cyclic hydrocarbons as cyclohexane.

Thereby, the high catalytic performance in the dehydrogenation of the cyclohexane for Pt(0.5 wt%)/ Al_2O_3 catalyst can be inferred as a high Pt–Al interaction of well dispersed Pt particles on the support, in line with CO-DRIFTS, TPR and XPS results. More importantly, the r_d rates show drastically decay with increasing the Pt loadings from 0.5 to 2.0 wt%, having the later solid with a very low Pt dispersion. In agreement, Pt loadings superior to 0.5 wt% experience a decreased Pt dispersion with lowest values for E_{app} and TOF, being the r_d/r_{SRM} of 0.2 for Pt(2.0 wt%)/ Al_2O_3 . This could be a reason for the appearance of agglomerations of the metal particles in the CO-DRIFTS, TPR and TEM observations, resulting in a lesser metal dispersion (D_{Pt}) and a lower number of converted CH_4 molecules, as well. Importantly, the reactions were carried out upon negligible external as well as internal heat and mass transfer limitations [19,22,23].

Catalytic results

Partial oxidation of methane (POM)

Fig. 6 shows the results of CH_4 conversion and H_2 , CO and CO_2 selectivities as a function of time on stream for POM reaction over the catalysts.

The Pt(x wt%)/ Al_2O_3 catalysts depict very high methane conversions (59–78%) at the beginning of the reaction, being more significant for that containing 2.0 wt% of Pt. Such an effect is in fact attributed to the good dispersion of Pt nanoparticles on the alumina support (CO-DRIFTS, TEM and cyclohexane dehydrogenation results). As found elsewhere, the small particle sizes of reduced metals dispersed on supports can be oxidized under a stream of oxygen diluted in nitrogen at 800 °C temperature; however, no sintering of the particles may occur in the first hours of the POM reaction [5,24]. The CH_4 conversions experience a decline with increasing the time on stream within 10 h (Fig. 6a) mostly due to coking (later shown by TEM of the spent catalysts).

Notably, the solids reach a plateau in their methane conversions after 10 h of time on stream. Besides, as the Pt loadings increase for more than 0.5 wt%, the Pt (x wt%)/ Al_2O_3 solids have an improvement in their performances, as expected. For instance, CH_4 conversion rises from 40 to 67%, when Pt loading is increased to more than 0.5 wt% in Pt (x wt%)/ Al_2O_3 series in 10 h of time on stream. Combined with the characterizations results and previous literature reports, lower CH_4 conversions are observed for Pt loadings lesser than 1 wt%, which is closely related to the presence of a lesser number of active sites for the adsorption of reactant molecules for the methane reforming reactions to take place [25–28].

On increasing the Pt loadings on Pt(x wt%)/ Al_2O_3 catalysts, the TOF obtained for POM reaction slightly decreases from 34.6 to 31.8 s^{-1} respectively for 0.5 and 1.0 wt% of Pt. The TOF decay is associated with the low dispersion of the Pt species

Table 3 – Activity coefficient, surface C/Al ratios of fresh and used catalysts on POM during 24 h of reaction.

Catalyst	$r_{\text{CH}_4-24\text{ h}} \times 10^{-4}$ ($\text{mol s}^{-1} \text{ g}_{\text{cat}}^{-1}$)	C/Al ^a 24 h	C 1s ^b
Pt(0.5 wt%)/ Al_2O_3	4.27	1.50	287.2
			285.7
			284.6
			283.7
Pt(1.0 wt%)/ Al_2O_3	6.82	0.55	288.5
			286.6
			285.2
			284.4
Pt(2.0 wt%)/ Al_2O_3	7.18	0.35	288.1
			286.4
			285.3
			284.4
			283.6

^a Surface C/Al ratio was determined by ratio between the peaks XPS intensity of C 1s and Al 2p for spent solids.

^b Samples used on partial oxidation of methane at 800 °C for 24 h.

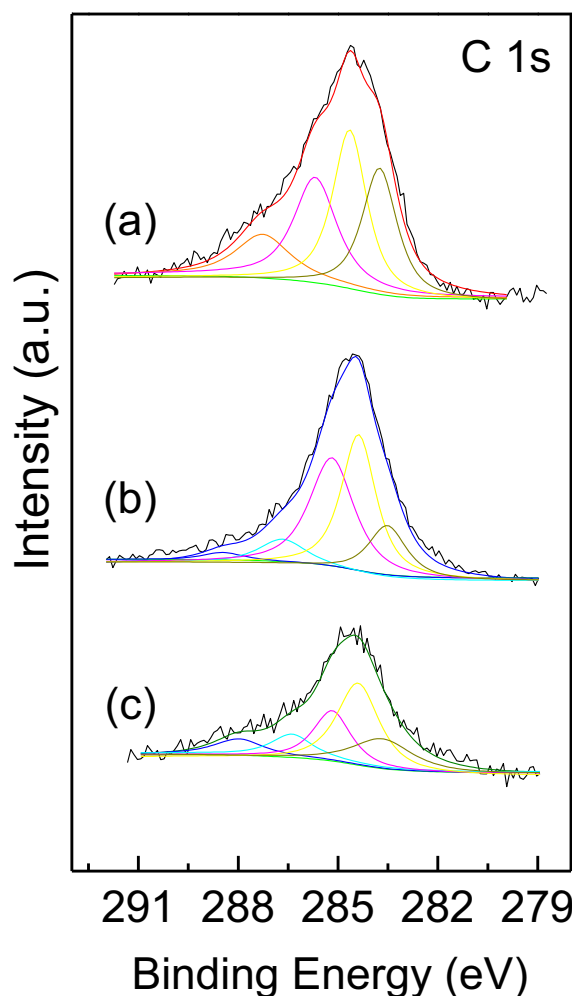
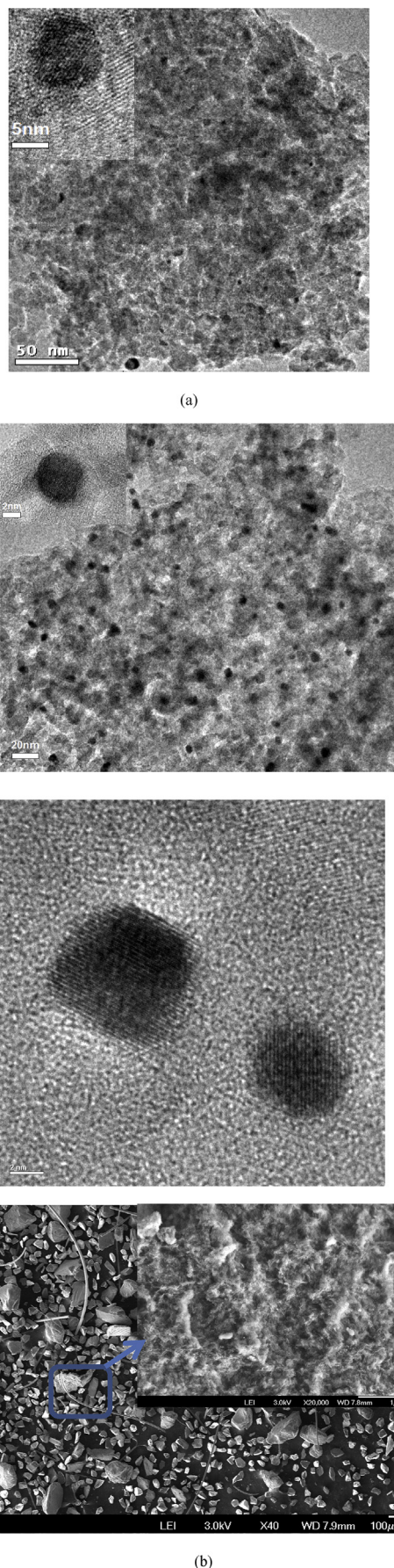


Fig. 7 – XPS C 1s core-level spectra of catalysts used during 24 h on POM reaction: (a) Pt(0.5 wt%)/ Al_2O_3 , (b) Pt(1.0 wt%)/ Al_2O_3 and (c) Pt(2.0 wt%)/ Al_2O_3 .



on the samples possessing more than 0.5 wt% of Pt. This does not corroborate with the CH_4 conversions data, which shows the solids possessing more than 0.5 wt% of Pt are the most active catalysts in POM, in spite of their low metal dispersion (TOF in POM and r_d in cyclohexane dehydrogenation reaction data). In agreement with this, the obtained facts indicate that the addition of platinum e.g., more than 0.5 wt% on the $\text{Pt}(x \text{ wt\%})/\text{Al}_2\text{O}_3$ catalysts gives mostly exposed active Pt nanoparticles surface species, despite the larger agglomeration of big Pt particles. Hence, the surface with solids possessing more than 0.5 wt% of Pt seems to be rich in active smaller Pt particles sites together with the agglomerated ones, which produces a lower TOF, but easily convert a higher number of CH_4 molecules compared to the other catalysts in 24 h of time on stream (Fig. 6a).

Thereby, the $\text{Pt}(x \text{ wt\%})/\text{Al}_2\text{O}_3$ surfaces are not capable of stabilizing Pt nanoparticles against sintering, as the Pt content is greater than 1.0 wt% and thus, a lesser dispersion is observed, despite the high number of active nanoparticles active prone to convert CH_4 .

The H_2 selectivity behavior of $\text{Pt}(x \text{ wt\%})/\text{Al}_2\text{O}_3$ catalysts (Fig. 6b) is found to be nearly similar to those observed for CH_4 conversion, being the direct route of POM reaction (I) occurrence almost constant after 10 h of the time on stream. In addition, upon decreasing Pt loadings to 2.0 wt%, the selectivity of H_2 increases and $\text{Pt}(2.0 \text{ wt\%})/\text{Al}_2\text{O}_3$ catalyst achieves 64% of H_2 production in 24 h.

The CO_2 selectivities (Fig. 6c) is below 48% for all the solids indicating that the reaction rather proceeds via the total combustion of methane (IV). In addition, lower Pt loadings give more CO_2 , which could confirm the fast CH_4 decay of $\text{Pt}(0.5 \text{ wt\%})/\text{Al}_2\text{O}_3$ and thus, its poor performance is due to carbon deposition deactivation via reaction (V). Regarding the CO selectivity (Fig. 6d), the solids produce high amounts of CO initially and then, it falls for $\text{Pt}(0.5 \text{ wt\%})/\text{Al}_2\text{O}_3$ and $\text{Pt}(1.0 \text{ wt\%})/\text{Al}_2\text{O}_3$ catalysts. Thereby, the solids possessing low Pt loadings are very selective to CO indicating that the steam and dry methane reforming reactions (II) and (III), respectively may take place instead of POM reaction. Additionally, the reverse water gas shift reaction-RGWS (reaction VI) and CO disproportionation, namely the Boudouart reaction (V) become predominant over $\text{Pt}(0.5 \text{ wt\%})/\text{Al}_2\text{O}_3$ and $\text{Pt}(1.0 \text{ wt\%})/\text{Al}_2\text{O}_3$ catalysts with consequent decrease of the hydrogen selectivity.



Therefore, the high selectivity to CO and H_2 displayed by $\text{Pt}(2.0 \text{ wt\%})/\text{Al}_2\text{O}_3$ clearly indicates the efficient stability of its Pt particles against sintering in 24 h of POM reaction, compared to that of $\text{Pt}(0.5 \text{ wt\%})/\text{Al}_2\text{O}_3$ and $\text{Pt}(1.0 \text{ wt\%})/\text{Al}_2\text{O}_3$ counterparts. Additionally, the $\text{Pt}(2.0 \text{ wt\%})/\text{Al}_2\text{O}_3$ catalyst

Fig. 8 – TEM images of spent $\text{Pt}(x \text{ wt\%})/\text{Al}_2\text{O}_3$ catalysts used on the partial oxidation of methane at 800°C for 24 h: (a) $\text{Pt}(0.5 \text{ wt\%})/\text{Al}_2\text{O}_3$ and (b) $\text{Pt}(2.0 \text{ wt\%})/\text{Al}_2\text{O}_3$. The HRTEM images are included.

shows better catalytic performance compared with other Pt dispersed on alumina catalysts under similar reaction conditions during 24 h of time on stream [4,36–38].

Spent solids characterizations by XPS, TEM and Raman measurements

XPS analyses are performed to further examine the element surface concentrations and oxidation states for spent catalysts. The relative atomic concentrations are summarized in Table 3 with the C1s core level spectra shown in Fig. 7.

As shown in Table 3, an increase in the carbon surface concentration is observed for spent Pt(x wt%)/Al₂O₃ catalysts, owing to the carbonaceous deposition on solid surfaces. Moreover, the relative C/Al atomic ratio is 1.50 for spent Pt(0.5 wt%)/Al₂O₃, which is indeed the highest among all catalysts studied. It is clear that the C/Al atomic ratios of Pt(2.0 wt%)/Al₂O₃ are quite low as compared to those for Pt(1.0 wt%)/Al₂O₃ and Pt(0.5 wt%)/Al₂O₃ catalysts. Although high Pt loadings on alumina could enable to sintering of these Pt particles, the heavy carbon deposition is alleviated on the catalyst surface by eventually liberating the active phase from filaments or whisker (carbon nanotubes) with oxygen from the reaction. In line with these results, Pt loadings >0.5 wt%

are highly active, as shown through the highest activity in POM reaction of ca. $7.18 \times 10^{-4} \text{ mol s}^{-1} \text{ gcat}^{-1}$ for Pt (2.0 wt%)/Al₂O₃ (Table 3), when comparing with to that of the solids with lower Pt loadings.

Furthermore, the C1s spectra are deconvoluted into two or three different kinds of surface carbon species (Fig. 7).

The binding energies (BE) observed for Pt(0.5 wt%)/Al₂O₃ are 287.2, 285.7, 284.6 and 283.7 eV. These peaks have been assigned as follows: (i) Pregraphite –like species at 283.5–283.3 eV (ii), the C–C or C–H bonds at 284.5–284 eV, (iii) C–OH or CxHy entities at 285.7–285.8 eV, (iv) the C–O–C bonds at 286.5 eV, (v) –C=O groups at 287.5 eV and the O–C=O species at 288.5 eV [29,30]. Besides the aforesaid BE, a small peak at 283.7 eV with 27% of the total peak area is assigned to filamentous carbon [31] for all catalysts. These carbon deposits are mainly caused by the following reactions [32]:



Especially in the case of Pt(2.0 wt%)/Al₂O₃, the solid surface is covered on amorphous carbon deposits, but oxygen from the reaction is able to burn the coke and this implies that its deactivation is alleviated in 24 h of reaction.

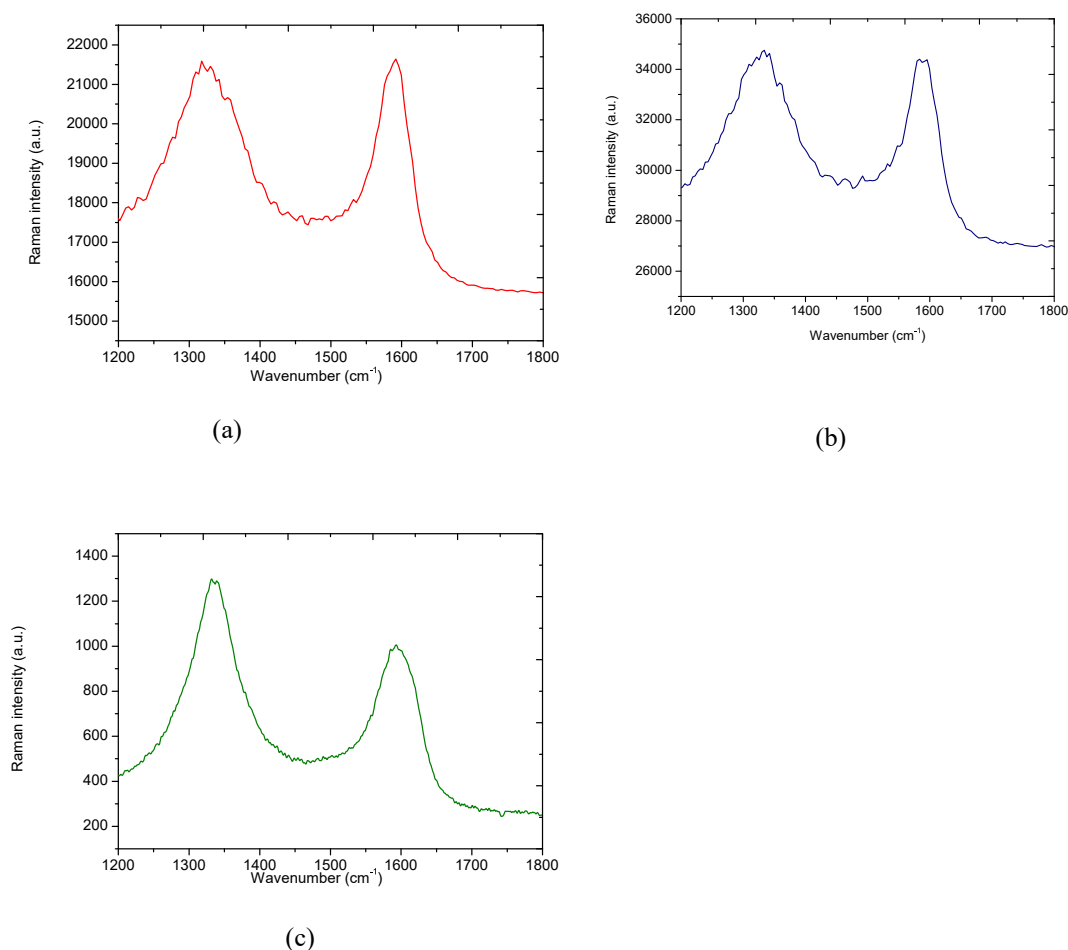


Fig. 9 – Raman spectra of the samples used on the partial oxidation of methane at 800 °C for 24 h: (a) Pt(0.5 wt%)/Al₂O₃, (b) Pt(1.0 wt%)/Al₂O₃ and (c) Pt(2.0 wt%)/Al₂O₃.

TEM images of selected spent samples are depicted in Fig. 8.

The Pt particles became bigger and moved to the surface, when increasing the Pt loadings, as shown by TEM image of the Pt(0.5 wt%)/Al₂O₃ (Fig. 8a). Moreover, the included HRTEM image suggests the presence of the (020) plane of Pt with d-spacing of 0.195 nm (inset Fig. 8a). Indeed, the sample possessing the lowest Pt content has the greater Pt particles size of ca. 10–15 nm, indicating the sintering of the Pt particles after the catalytic test. This is consistent with our catalytic test results that depicts a low catalytic performance for former solid (Fig. 5) and agrees with the C/Al ratios obtained by XPS (Table 3), which suggest the higher amount of carbonaceous deposits on the former catalyst. The findings state that whisker and graphite carbon decay the catalyst performance in methane reforming reactions and usually Pt is the active element that is expected to sintering [28]. All these facts contribute to the poor performance of Pt(0.5 wt%)/Al₂O₃ catalyst comparing with the Pt(2.0 wt%)/Al₂O₃.

Examinations of the images with increment in the Pt loadings evidences the Pt particles growth of Pt(2.0 wt%)/Al₂O₃ (Fig. 8b, TEM image) with and their consequent agglomeration. The (020) plane of Pt shows d-spacing of 0.195 nm [28]. These particles seems to be bigger those of Pt(0.5 wt%)/Al₂O₃ (HRTEM image in Fig. 8b) as a consequence of the sintering of the solid, after the reaction. However, no heavy whiskers and filaments of carbon formation are seen in the included SEM image (Fig. 8b). It may explain the higher catalytic performance of Pt(2.0 wt%)/Al₂O₃, in comparison with the low Pt loadings counterparts.

Raman measurements of the spent catalysts are performed to show the type of carbon species deposited on the spent samples (Fig. 9).

It is clear from Fig. 9 that the solids used in the POM reaction shows two Raman bands at 1350 and 1600 cm⁻¹. This result confirms that the carbon deposition occurs over all solids studied. Moreover, the Raman band at about 1300 cm⁻¹ is related to the D band from disordered carbon accumulation on the catalysts whereas the G band at around 1600 cm⁻¹ is due to the graphite carbon structure e.g., filamentous carbon species deposition [38–40].

The relative intensity of the G band is higher than the D one for the samples possessing Pt content inferior to 1.0 wt%. This is an indication that the degree of disorder carbon deposition is high on these samples with the consequent deactivation by filamentous carbon species. Thus, the amount of carbon accumulated on Pt(0.5 wt%)/Al₂O₃ and Pt(1.0 wt%)/Al₂O₃ catalyst surface is higher than that of Pt(2.0 wt%)/Al₂O₃, in agreement with TEM and XPS results. Indeed, the I_D/I_G ratio of Pt(0.5 wt%)/Al₂O₃ and Pt(1.0 wt%)/Al₂O₃ spent catalysts are respectively 0.80 and 0.74 and confirms their low catalytic performance compared with performance as compared with the spent Pt(2.0 wt%)/Al₂O₃ counterpart (I_D/I_G of ca. 0.63).

At present, POM reaction is governed by two mechanistic considerations i.e., the direct route ensuring an initial formation of CO and H₂, while the indirect ones involve the CH₄ activation to form steam and CO₂ by reforming of CH₄ [34,35]. Based on these considerations and the observed results, it can be pointed out that the C–H activation on the surface of Pt nanoparticles is the limiting POM reaction step. However, an

increased Pt dispersion is only observed for samples having low Pt loadings, which reflects in their nanosized features and increased the rate of C–H bond cleavage. With respect to the lower Pt loadings, a lesser availability of CH₄ molecule to the active site due to the sintering and coking is observed in 24 h of reaction and thus, a low catalytic performance is observed. Simultaneously, high Pt loadings e.g., Pt(2.0 wt%)/Al₂O₃, avoid the deactivation of the solid by carbon heavy accumulation and sintering as well.

Conclusions

Varying the Pt loadings and the particles sizes strongly affect the stability of Pt(x wt%)/Al₂O₃ catalysts in POM and dehydrogenation of cyclohexane reactions. An increase in the Pt loadings e.g., more than 0.5 wt% on the catalysts gave mostly exposed active Pt⁰ surface particles, despite the larger agglomeration of big Pt clusters resulting in an improved methane conversion. The high Pt loadings of ca. 2.0 wt% on alumina could enable to sintering of these Pt particles. However, the heavy carbon deposition was alleviated on the catalyst surface by liberating the active phase from heavy carbon deposition with oxygen from the reaction, in comparison with the low Pt loadings counterparts.

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