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Water Gas Shift Reaction over Pt-CeO_2 Nanoparticles Confined within Mesoporous SBA-16

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Abstract

Novel nanocomposite catalysts for single step Water Gas Shift Reaction (WGSR) were prepared by deposition-precipitation and impregnation of Pt-CeO_2 nanophases onto an ordered mesoporous silica support featuring a cubic arrangement of mesopores (SBA-16 type). The highly interconnected porosity of the SBA-16 developing in three-dimension (3D) provides a scaffold which is easily accessible to reactants and products by diffusion. The textural and morphological properties of the final catalyst were affected by the procedure utilized for dispersion of the nanophases onto SBA-16. Catalysts prepared by deposition-precipitation present highly dispersed nanocrystalline CeO_2 on the surface of SBA-16 and retain high surface area, high thermal stability and high Pt accessibility. Catalysts prepared by impregnation show improved Pt-CeO_2 interaction but a more significant decrease of surface area compared to pure SBA-16, due to the confinement of the CeO_2 crystallites within the mesoporous matrix.

As a result, catalysts prepared by deposition-precipitation are effective for WGSR under working conditions in the high temperature range (around 300-350 °C), whereas catalysts prepared by impregnation are suitable for the process operative at low temperature (LT-WGSR). Our results point out that catalyst preparation procedures can be used to optimise the performance of heterogenous catalysts, by controlling the CeO_2 crystallites size and optimizing Pt-CeO_2 contact by embedding. Improved thermal and chemical stability was achieved using a mesoporous scaffold.

Keywords:

Mesoporous silicas, nanoparticles, ceria, platinum, catalysis

1. Introduction

The Water-Gas Shift Reaction (WGSR):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^0_{298} = -41.4 \text{ kJ mol}^{-1}$$

is a key process in the modern chemical industry, since it allows to control the H_2/CO_X ratio and the CO_X composition starting from the syn-gas produced by reforming processes. Low H_2/CO ratio is required for Fischer-Tropsch synthesis of liquid fuels and for hydroformilation reactions, while $H_2/CO/CO_2$ mixtures are required for methanol synthesis. On the other hand, applications that use large amounts of pure H_2, such as NH_3 synthesis, oil refining and hydrogenation processes involved in fine chemical production, require very high starting H_2/CO_2 ratios in order to effectively remove CO_2 by absorption into basic solutions. In the last decades, H_2 production attracted great attention for the development of upgrading processes in biorefineries (e.g. hydrodeoxygenation) and in view of the possible use of large amounts of H_2 as energy vector, in combination with fuel cells technology. In the last case, the diffuse energy production employing Polymer Electrolyte Membrane Fuel Cells (PEMFCs) will require an extremely low CO content (usually below 10 ppm) to avoid poisoning of Pt-based anode electrocatalysts.[1] It must be underlined that, being the WGSR an equilibrium reaction, the CO content at the exit of the WGSR reactors is still too high and a further purification process is required. This is the so-called PROX (PReferential OXidation of CO in the presence of H_2).

WGSR is an exothermic reaction and therefore thermodynamically limited at high temperatures and kinetically limited at low temperatures. Because of that, the production of H_2 in industrial large-scale plants involves a two-step process: a high temperature (HT-WGSR) step (350 – 450 °C) in presence of Fe_2O_3-Cr_2O_3 based catalysts and a low-temperature (LT-WGSR) step (180 – 250 °C) in presence of Cu-ZnO catalysts. The conventional Cu-ZnO - based LT-WGSR catalysts present severe limitations, such as low activity at the relevant fuel cell temperature range, pyrophoric nature and weak stability under cyclic operation.[2] Recently, research has focused on noble metals (Pt, Ph, Ru, Au, Pd) supported on reducible oxides (CeO_2, TiO_2) as highly active WGSR catalysts.[3] Among all the systems studied, Pt-CeO_2 is regarded as the most promising catalyst due to CeO_2 ability to undergo rapid (Ce(IV)/Ce(III)) reduction and oxidation cycles, further promoted by the addition of Pt on the CeO_2 surface, with consequent enhancement of the WGS activity, in particular in the low temperature process.[4] The redox and catalytic properties of ceria are also strongly dependent on particle size, a decrease in particle size being associated to an increase of density of oxygen defects and hence an enhancement of the number of active sites for gas-solid catalysis.[5,6] However, pure ceria has a poor thermal stability and undergoes sintering at high temperatures.[7,8,9] To overcome this problem, CeO_2 is usually doped with another metal oxide (generally ZrO_2 or lanthanide oxides)[5] or is dispersed on a high surface area thermally stable support (such as Al_2O_3)[5,10,11]. Recently, dispersion on a silica matrix with ordered mesoporous structure and hexagonal symmetry such as MCM-41 type[12] and SBA-15 type[6,12,13] has been proposed as a strategy to improve thermal stability of nanocrystalline ceria. Silica-supported nanocrystalline ceria materials are of particular interest in catalysis, since the mesoporous silica supports provide thermal stability as well as high surface area. So far, only ordered mesoporous silica supports with a hexagonal porous geometry have been used to stabilize CeO_2. In this work, we address the design of novel catalysts for LT-WGSR by dispersing Pt-CeO_2 nanophases onto an ordered mesoporous silica support with a cubic arrangement of mesopores (SBA-16 type) developing in three-dimensions (3D). The highly interconnected pores provide a scaffold easy accessible from all directions to reactants and products by diffusion.[14] Additionally, the SBA-16 scaffold presents high thermal stability,[15] thick walls and enhanced resistance to local pore blockage,[16] making it very attractive for nanoparticles dispersion.[17] It should be pointed out that to successfully produce the cubic arrangement of pores typical of SBA-16 type silicas, a careful adjustment of the synthetic conditions needs to be achieved.[18] For this reason the literature on SBA-16 is more limited than that on SBA-15. However, very recently the potential of SBA-16 as support for copper-based catalysts for the WGSR has been investigated.[19]

In this work, SBA-16 type silica is used as a support for CeO_2 and Pt nanophases with the aim of designing innovative catalysts for LT-WGSR. The catalysts synthesis was designed to confine both CeO_2 and Pt nanoparticles within the mesoporous silica scaffold. This allows us to maximize the contact between the two nanophases and to hinder their sintering, finally leading to high catalytic activity. Different wet chemistry routes were tested in order to achieve an efficient dispersion of the CeO_2 and Pt nanophases in the SBA-16. A 1 wt% loading of Pt was selected based on recent findings on Pt-based catalysts for WGS process,[7] whereas two different CeO_2 loading were investigated (10 and 20 wt%). The samples were characterized by Transmission electron microscopy (TEM), X-ray powder diffraction (XRD), N_2 physisorption and H_2 chemisorption. Catalytic activity results indicate that the confinement within SBA-16 pores is effective in stabilizing CeO_2 and maximizing Pt-CeO_2 interactions.

2. Experimental

2.1 Catalyst preparation

Pt-CeO_2/SBA-16 catalysts were prepared either by deposition-precipitation (DP) or by co-impregnation (IMP) of dodecanthiol-protected PT nanoparticles (Pt-DT) and of cerium(IV) tetrakis(decyloxide) ($Ce(OR)_4$) on the SBA-16 support. The details of the preparation of Pt-DT nanoparticlesand of $Ce(OR)_4$ are reported in the ESI†.

2.1.1 Synthesis of pure SBA-16 silica.

The synthesis of pure SBA-16 was performed according to a procedure[18] which makes use of Pluronic F127 (P127, Aldrich), a high molecular weight (M_{av}=12600) block copolymer formed by a sequence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) units with high EO/PO ratio (EO_{106}-PO_{70}-EO_{106}), as a structure directing agent. 4.0 g of P127 were added to a mixture of 30 g of water and 120 g HCl 2M under stirring at room temperature. Tetraethoxysilane (8.5 g, TEOS, Aldrich 98%) was then added to the solution, which became opalescent due to the precipitation of the SBA-16 after about 30 minutes. The solution was left under stirring at room temperature for 20 hours and then aged at 80 °C for 2 days. The precipitate of SBA-16 was separated from the mother solution by centrifugation, washed with distilled water and dried at room temperature. The organic template (P127) was removed by calcination of the dried powder in static air at 500 °C with a heating rate of 1 °C min^{-1}, and hold at the final temperature for 6 hours.

2.1.2 Synthesis of Pt-CeO_2/SBA-16 by DP route

Two Pt-CeO_2/SBA-16 samples were prepared by deposition-precipitation method according to reference 13 modified for SBA-16. CeO_2 was deposited into the previously prepared SBA-16 by precipitation of cerium hydroxide. To this end, a solution of cerium (IV) ammonium nitrate (either 0.63 g or 1.26 g in 100 mL) and urea (either 1.02 g or 2.04 g) was added to 1.6 g of SBA-16 in a flask thermostated at 90 °C. The suspension was magnetically stirred for 150 minutes, cooled to room temperature and then filtered. The sample was then washed three times with deionized water, dried at 120 °C for 24h and calcined at 500 °C for 4h. Pt was deposited by addition of 10mL of an aqueous solution of H_2PtCl_6 into 1 g of the previously prepared CeO_2/SBA-16 to obtain a final Pt content of 1 wt% with respect to the total mass of catalyst. The solution was stirred for 1hour at room temperature and 4 hours at 80 °C. The final sample was filtered and dried at 120 °C overnight and calcined at 500 °C for 4 hours. The two samples obtained varying the CeO_2 content (10 and 20 wt%) will be hereafter indicated as DP_Pt/CeO_2(10%)/SBA-16 and DP_Pt/CeO_2(20%)/SBA-16.

2.1.3 Synthesis of Pt-CeO_2/SBA-16 by IMP route

Two Pt-CeO_2/SBA-16 were obtained by impregnation of SBA-16 with a solution containing Pt-DT nanoparticles and $Ce(OR)_4$ in toluene, whose synthesis is reported in the ESI (sections S1.1 and S1.2†). Briefly, 1.00g of SBA-16 was degassed overnight at 250 °C to remove adsorbed water and then suspended into 10 mL of toluene. Pt-DT and $Ce(OR)_4$ were mixed together in toluene and added dropwise to the SBA-16 suspension. After stirring for 5h, the solvent was slowly removed by evaporation at reduced pressure. After drying at 120 °C overnight, the powders were calcined in static air at 500 °C for 5h. These two catalysts will be hereafter indicated as IMP_Pt@CeO_2(10%)/SBA-16 and IMP_Pt@CeO_2(20%)/SBA-16.

To improve the diffusion of Pt-DT and $Ce(OR)_4$ within the mesopores of SBA-16, the surface of SBA-16 was treated with triethoxyoctyl silane (TEOOS, Sigma-Aldrich, 97.5) to obtain a hydrophobic support. After degassing the synthesized SBA-16, the support was suspended in 25 mL of toluene, 523 µL of TEOOS was added and the suspension was refluxed overnight. The powder was recovered by centrifugation, washed 3 times with 10 mL of toluene and vacuum dried at room temperature. Impregnation with Pt-DT and $Ce(OR)_4$ was performed using the same procedure adopted for the IMP_Pt@CeO_2(XX%)/SBA-16 materials described above. These two catalysts will hereafter be labeled as IMP_Pt@CeO_2(10%)/H-SBA-16 and IMP_Pt@CeO_2(20%)/H-SBA-16, where the symbol H indicates that the SBA-16 was made hydrophobic before impregnation.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded in the range of 15°- 85° (2ϑ) on a Panalytical Empyrean diffractometer equipped with Cu Kα source, a graphite monochromator on the diffracted beam, and a X'Celerator linear detector. The average size of the CeO_2 nanoparticles was estimated using the Scherrer formula, $t = 0.91\lambda/(B\cos\vartheta)$, where t is the crystallite size, λ is the incident radiation wavelength, ϑ is the Bragg angle and B is the full-width at half-maximum of the diffraction peak (corrected for instrumental broadening).

Textural characterization was performed by N_2 adsorption-desorption measurements at liquid nitrogen temperature recorded on a Micromeritics ASAP2020. Prior to analysis, samples were outgassed under vacuum at 200 °C. Surface area were estimated using the Brunauer-Emmett-Teller (BET) model,[20, 21] pore size and pore volumes were estimated using the Non-Local Density Functional Theory (NLDFT) using the Tarazona model for cylindrical pores.[22]

H_2 chemisorption experiments were carried out using a Micromeritics ASAP 2020C. Typically, 150mg of the fresh material were loaded in a U-shaped reactor and reduced by flowing H_2(5%)/Ar (40 mL min^{-1}) at 200 °C for 1h. Adsorbed hydrogen is then removed by evacuation at 300 °C for 6h. Chemisorption analysis was performed firstly at -90 °C (liquid/solid acetone bath) dosing H_2 (2 – 400 torr). Then, the sample was again evacuated at 300 °C for 6h and the chemisorption analysis was repeated at 35 °C. In both the cases, the contribution of physisorption was subtracted by extrapolation to zero of linear part of the isotherms. In the case of the aged samples, the sample was speedily transferred into the chemisorption reactor after the catalytic tests and only evacuated at 350 °C for 6h. In this case, the chemisorption analysis was performed only at -90 °C.

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX) was performed on a Hitachi S-3400N microscope equipped with a W gun, a Secondary

Electrons detector and an Oxford Instruments "X-max 80" EDX spectrometer. Samples were deposited on sticky carbon tape mounted on a 15mm Aluminium stub.

Transmission Electron Microscopy (TEM) images were recorded on a Hitachi H-7000 Microscope equipped with a W thermoionic filament and operating at 125 kV. The catalysts were ground in an agate mortar and deposited on a carbon-coated copper grid for observations. The images were acquired using an AMT DVC CCD camera in bright field (bf) and dark field (df) mode; selected area electron diffraction (SAED) pattern were acquired with a camera length of 20 cm.

2.3 Catalytic activity measurements

WGSR activity tests were performed in a U-shaped tubular reactor at atmospheric pressure, using a reaction mixture containing CO (2.0%) + H_2O (10.0%) in Ar. The gas hourly space velocity (GHSV) was set at 50000 mL g^{-1} h^{-1} using a total flow rate of 40.7 mL min^{-1} and 48.9 mg of the powdered catalyst. A granular quartz bed was put in the reactor to support the powdered catalyst while a 3 mm layer of granular quartz was put above the catalytic bed to pre-heat the gas flow. The flows of CO and Ar were adjusted using mass flow controllers while 3 μL min^{-1} of H_2O was introduced in the gas flow by means of a GASTight syringe, controlled by an infusion pump. Vaporization of H_2O was ensured by heating of the reactivity line at 120 °C by adequate heating tapes. The composition of the effluent from the reactor was monitored on-line using a Hiden HPR20 mass spectrometer.

Before each catalytic test, the catalysts were cleaned by a treatment in 40 mL min^{-1} of O_2 (5.0%) in Ar at 400 °C for 30 min. After cooling to 150 °C, the gas flow was switched to pure Ar for 1 h to remove O_2 from the system. Light-off experiments were performed introducing the reaction mixture in the reactor and stabilizing the signals for 1 h, before increasing the temperature up to the desired value at the rate of 2 °C min^{-1}. Aging of the catalysts were performed maintaining the reactor at the desired temperature for the desired time, before cooling down to 150 °C at the rate of 2 °C min^{-1}.

3. Results and Discussion

The XRD patterns of the pure SBA-16 silica support and of the synthesized catalysts are shown in Fig. 1. The pattern of pure SBA-16 (Fig. 1a) is typical of amorphous silica and only shows a broad halo at 2ϑ ~ 20-30°. The XRD patterns of the catalysts are similar and show broad peaks detectable in the region 2ϑ ~ 28-80° ascribed to the cubic fluorite-type structure of CeO_2 (PDF 034-0394), on top of the SBA-16 background (Fig. 1b-1g). As expected, the intensity of the peaks is higher for the catalysts containing 20 wt% of CeO_2 compared to those containing 10 wt%. The broad XRD reflections are indicative of nanosized CeO_2, having average nanocrystal sizes in the range of 2-4 nm, as calculated by the Scherrer equation (Table 1). These results indicate that nanocrystalline ceria has been effectively stabilized into SBA-16 with 10 and 20 wt% loading. In all the materials investigated, no reflections ascribed to Pt-related phases can be detected, as expected for the low metal loading and the small size of the Pt nanoparticles,[23] as already reported for various Pt-CeO_2 systems.[2,3,24-27]

The texture of the pristine SBA-16 and of the prepared materials was studied by N_2 physisorption at the liquid nitrogen temperature. According to the IUPAC classification, the N_2 physisoprtion isotherms of pure SBA-16 (Fig. 2A) can be classified as type IV isotherm with a H2 type hysteresis, typical of materials containing ink-bottle mesopores and indicative of a cage-like cubic porous structure. The N_2 physisorption isotherms of the materials prepared by DP (Figs. 2B and 2C), indicates that the mesoscopic cubic order is preserved after the calcination treatments needed to stabilize the CeO_2 and Pt components, and that the pores of SBA-16 are not significantly occluded by the deposition of the active phase. The isotherms of the samples prepared by co-impregnation on the bare SBA-16 (Figs. 2D and 2E) and on the hydrophobic H-SBA-16 (Figs. 2F and 2G) show a significant decrease in the overall adsorbed amount of N_2 with respect to the pristine SBA-16 support.

The textural parameters calculated by analyzing the physisorption data are summarized in Table 1. SBA-16 has a very high surface area and pore volume, with pore size distribution centered at 6.5 nm, in accordance with the literature.[28,29] After loading of the active phase, the differences in textural properties are strongly dependent on the preparation route adopted and generally more evident for samples having a 20 wt% CeO_2 loading. For almost all samples, a decrease in surface area and pore volume is observed, although the pore size distribution is only marginally affected. The deposition of the active phase by DP causes the smallest change in surface area and pore volume while the IMP route results in a significant decrease of the accessible surface area and pore volume. The decrease in pore volume is more evident in the samples prepared using H-SBA-16 and can be associated with the occlusion of a significant fraction of pores. Notably, the process to make the support hydrophobic has been introduced in the preparation procedure in order to maximize the diffusion of hydrophobic Pt-DT and $Ce(OR)_4$ precursors within the SBA-16 texture. It should be pointed out that plugging of the pores with the catalysts remaining on the SBA-16 surface can be excluded since this would be accompanied by a drastic decrease of the surface area which was not observed for any of the samples. It should also be noted that DP_Pt/CeO_2(20%)/SBA-16 has a surface area and pore volume very similar (within the experimental error) to the pure SBA-16 sample, while DP_Pt/CeO_2(10%)/SBA-16 has a slightly lower surface area.

The mesoporous structure of the catalysts and the dispersion of the nanostructured active phases in the SBA-16 matrix were investigated by TEM. Representative TEM images are reported in Fig. 3 for DP_Pt/CeO_2(10%)/SBA-16 and DP_Pt/CeO_2(20%)/SBA-16, in Fig. 4 for IMP_Pt@CeO_2(10%)/SBA-16 and IMP_Pt@CeO_2(20%)/SBA-16 and in Fig. 5 for IMP_Pt@CeO_2(10%)/H-SBA-16 and IMP_Pt@CeO_2(20%)/H-SBA-16. A highly ordered arrangement of mesopores can be seen in all the samples, confirming that the SBA-16 scaffold is preserved in the final material, independently from the preparation route employed, in agreement with the physisorption analysis results. The samples are composed of spherical nanoparticles homogeneously dispersed within the SBA-16 mesoporous matrix. CeO_2 nanoparticles are particularly evident in the dark field images, in which they appear as bright spots. The SAED patterns of CeO_2 in all the samples show the rings corresponding to the fluorite CeO_2 structure, confirming that the nanoparticles crystalline (ESI, Fig. S1†). The TEM images show that the CeO_2 nanoparticles are well dispersed and confined in the SBA-16 matrix. In particular, in DP_Pt/CeO_2(20%)/SBA-16 (Figs. 3C/D and Fig. S2) CeO_2 nanocrystals smaller than the size of the SBA-16 pores are clearly visible both in the bright field images as dark spots and in the dark field images as bright spots. On the other hand, the CeO_2 nanoparticles in the samples prepared by co-impregnation seem to be less evident compared to the corresponding DP samples. This could be justified by either a less homogeneous dispersion of the nanoparticles in the matrix or by their confinement within the SBA-16 scaffold which would make them more difficult to be detected because of the thickness of the sample under investigation. The presence of Pt nanoparticles cannot be detected in any of the materials, because of Pt low loading and high dispersion into the CeO_2-SBA-16 matrix.[23] Further information on the morphology of the catalysts and on the dispersion of the nanostructured active phases in the SBA-16 matrix were investigated by SEM coupled by EDS, as reported in the ESI (Fig S3†**)**. As can be observed from SEM images, no CeO_2 aggregates have been observed outside the SBA-16 scaffold, indicating that the active phase is deposited within the mesoporous structure of the SiO_2 scaffold.

H_2 chemisorption analysis was employed to assess the accessibility of the Pt phase and the interaction between the Pt nanoparticles and the CeO_2 promoter. It was performed at -90 °C and 35 °C, with results summarized in Table 2. In agreement with previous H_2 chemisorption studies on noble metal nanoparticles supported on CeO_2-based materials[30,31], activated H atoms are spilled over the reducible oxide inducing the so-called “reversible reduction” of the promoter.[32] The reversible reduction of CeO_2 results in the conversion of the more superficial Ce(IV) to Ce(III) and the formation of superficial OH groups, which allow the H hopping and diffusion on the surface.[32]

The transfer of activated H atoms is strongly inhibited lowering the analysis temperature [30,31]. In this study, the H/Pt value measured at -90 °C is used to determine the fraction of accessible Pt atoms. The results obtained indicate that Pt accessibility depends both on the CeO_2 loading and on the preparation method. A slightly lower accessibility of surface Pt is observed for the materials with the higher CeO_2 content; however, the preparation method has the most prominent effect on accessibility, which is significantly enhanced in the samples prepared by DP route, independently from the CeO_2 loading. These results can be rationalized considering that the platinum precursor is impregnated after deposition of CeO_2 by deposition-precipitation on SBA-16 support. On the other hand, the co-impregnation route could lead to a partial occlusion of Pt nanoparticles within the CeO_2 nanocrystallites, in a similar manner to what observed for Pd@CeO_2/Si-Al_2O_3 prepared by self-assembled core-shell units.[33]

The H/Pt value measured at 35 °C includes the amount of H spilt over reducible CeO_2. Therefore, the ratio between H/Pt value measured at 35 °C and the one measured at 90 °C (R in Table 2) can be considered as an indication of the interaction between Pt and CeO_2 nanoparticles. All the H/Pt values measured at 35 °C are significantly higher than the values measured at low temperature and, notably, higher than 1, indicating that H is effectively spilt over the CeO_2 surface. Higher H/Pt values have been obtained, for each preparation method, with the materials with the higher CeO_2 content, in agreement with the more extended reducible surface available to accommodate OH groups. On the other hand, for the same CeO_2 loading, the preparation method has a strong influence on the hydrogen chemisorption capacity of the samples. The materials prepared by DP show the lowest H_2 chemisorption capacity although the Pt accessibility is the highest. These results indicate that the Pt-CeO_2 interaction is not optimal in the DP samples, with a significant fraction of Pt nanoparticles deposited onto free SBA-16 surface being not in direct contact with CeO_2 nanoparticles. The samples prepared by impregnation of SBA-16 with Pt-DT nanoparticles and $Ce(OR)_4$ show higher H_2 chemisorption capacities and better abilities to spill activated H onto the CeO_2 surface, despite the lower Pt accessibility and surface area. The impregnation methodology was designed in order to obtain Pt nanoparticles embedded into a matrix of CeO_2 crystallites, with the aim of maximizing the Pt-CeO_2 interaction. The spillover is further enhanced in the samples impregnated on the hydrophobic H-SBA-16 surface, indicating that this treatment allows the best distribution of the Pt and CeO_2 components.

3.1 WGSR activity

The CO conversion in consecutive reaction experiments over the synthesized catalysts are presented in Figs. 6-8. CO conversion increases with increasing temperature, until the thermodynamic equilibrium is reached. The stability of the present catalysts was evaluated by simulated fast aging of the catalysts by prolonged treatment under reaction conditions at 350 °C. The light-off temperatures (T_{50} – corresponding to 50% of CO conversion) and the lower temperature at which the chemical equilibrium is reached (T_{EQ}) are summarized in Table 3. Notably, no CO conversion was observed during blank experiments (reactor containing only the quartz bed and the thermocouple), while a Pt/SBA-16 sample, not containing CeO_2, showed only very poor catalytic activity, leading to CO conversion of 15% at 350 °C (ESI Fig. S4†).

The fresh DP samples (Fig. 6) showed no activity at 150 °C while increasing the temperature the chemical equilibrium is reached around 290 °C, irrespectively to the CeO_2 content. The DP_Pt/CeO_2(10%)/SBA-16 sample revealed a slight increase of activity in light-off experiments after aging for 16h, being unmodified by further 20 hours of aging. On the other hand, the DP_Pt/CeO_2(20%)/SBA-16 showed comparable and stable activities during the consecutive aging treatments.

Significantly higher catalytic activities were observed for the IMP materials, with the best performances demonstrated by the H-SBA-16 supported catalysts. The fresh IMP_Pt@CeO_2(10%)/H-SBA-16 and IMP_Pt@CeO_2(20%)/H-SBA-16 catalysts showed remarkable CO conversion at 150 °C (18 and 32%, respectively – Fig. 8). Despite the lower surface area and lower accessibility of Pt nanoparticles with respect to DP catalysts, the enhanced performances of the materials prepared by impregnation can be related with the more efficient interaction between the Pt nanoparticles and the CeO_2 promoter, as highlighted by H_2 chemisorption experiments. In agreement with this, the oxidation of CO has been demonstrated to be strongly dependent from the extension of the Pt-CeO_2 interface.[34]

Apparent activation energies (E_{att}) values ranging from 50 to 80 kJ mol^{-1} were calculated from CO conversion results during WGSR tests performed on the fresh material for all the investigated catalysts. These values are in good agreement with the results previously reported for Pt supported on reducible (CeO_2, CeO_2-ZrO_2)[35,36] and non-reducible oxides (ZrO_2, Al_2O_3).[35,37]

After simulated aging of the impregnated catalysts at 350 °C for 16 and 36 h, some deactivation occurred, as evidenced by the shift of the light-off temperatures to slightly higher values (~ 30 °C). Considering that the operative temperature of a WGSR catalyst should be quite close to the temperature at which the chemical equilibrium is reached, to further investigate the stability of the impregnated catalysts, IMP_Pt@CeO_2(10%)/SBA-16 and IMP_Pt@CeO_2(20%)/H-SBA-16 were aged under reaction condition at the T_{EQ} observed during the first light-off experiment (230 and 200 °C, respectively). Even after a 60 hours total aging time, the aged IMP_Pt@CeO_2(20%)/H-SBA-16 showed comparable light-off curves to the fresh catalyst, while the IMP_Pt@CeO_2(10%)/H-SBA-16 showed only a slight deactivation (ESI Fig. S5†).

The deactivation of Pt/CeO_2 catalysts is usually related with sintering of Pt nanoparticles[38] or with the adsorption of intermediates, mainly formates, on the active sites.[39] The latter is usually recognized as a major cause of deactivation at lower temperatures (below 300 °C), when formates are spectators of the reaction ad accumulate on the catalyst surface.[39] At higher temperature, formates are further converted and become intermediates in the catalytic process,[39] while sintering of Pt is considered the main way to catalyst deactivation.[38] In order to hinder Pt sintering, hierarchical Pt@CeO_2/Si-Al_2O_3 were prepared from self-assembled core-shell nanoparticles,[40] obtaining stable catalytic activity after pre-treatment of the catalyst at 500 °C. Differently from Pt, Pd@CeO_2/Si-Al_2O_3 demonstrates a fast decrease of the catalytic activity,[40,41] mainly because of an electronic influence due to reduced CeO_{2-x} and the partial occlusion of Pd nanoparticles within CeO_{2-x} crystallites.[41] To overcome these problems, Pd@CeO_2/MWCNT hybrid materials have been synthesized, observing that the balance between the organic and inorganic components favors their electronic interaction, finally leading to stable catalytic performances in WGSR.[42]

To investigate the origin of deactivation observed on the Pt/CeO_2 catalysts supported on SBA-16, the materials after catalytic tests have been characterized in detail in the view to highlight differences induced by prolonged aging under WGSR conditions. Also in this case, SEM coupled with EDX does not evidence segregation of the Pt/CeO_2 active phase outside the SBA-16 (see ESI Fig. S6†). The surface area of the materials subjected to the severe simulated aging at 350°C under WGSR significantly decreases with respect to the fresh materials (see ESI Table S1† and Fig. S8†). Notably, the extent of this sintering phenomenon is lower in the case of the catalysts tested under prolonged aging under realistic LT-WGSR (200 – 230 °C) (see ESI Table S1†). The most important modification highlighted by XRD analysis (Fig. S7†) is the presence of a broad (but detectable) peak at $2\vartheta \sim 40°$, corresponding to the main reflection of Pt. This reflection is present in all the aged samples, in a different extent depending on the material composition and preparation, being the most intense in the IMP_Pt@CeO_2(XX%)/H-SBA-16 materials. This result suggests that the Pt nanoparticles undergo a partial sintering and/or crystallization process during aging under WGSR. Notably, this phenomenon does not depend on the treatment temperature, being comparable for samples after severe simulated aging at 350 °C and prolonged aging under LT-WGSR (200 – 230 °C). In agreement with this, the H/Pt values measured by H_2 chemisorption analysis at -90°C (see ESI Table S2†) are lower than those measured for the fresh materials. The decrease ability/accessibility of Pt to H_2 can be due to a combination of different phenomena, including partial sintering, occlusion of Pt nanoparticles by the sintered support and by some extent of electronic strong metal support interaction (SMSI). Also in this case, the decrease of H/Pt values is less important in the case of the catalysts aged under LT-WGSR conditions. On the basis of these considerations, the deactivation of the present impregnated catalysts is expected to take place following different mechanisms depending on the aging temperature. The very limited deactivation observed during aging under LT-WGSR (see ESI Fig. S4†) can be related essentially to deposition of intermediates on the active sites of the catalysts. In agreement with this, deactivation is moderate and is less evident in the materials designed for maximizing the Pt-CeO_2 interaction by confinement within the nanometric pores of the SBA-16 scaffold. In this case, deactivation by electronic influence of reduced CeO_{2-x} is less important, in agreement with the characterization results of the aged catalysts and previous studies on H_2 and CO chemisorption on Pt/CeO_2 [43] and Pt/CeO_2-ZrO_2 [30] reduced at various temperatures. In any case, the IMP_Pt@CeO_2(20%)/H-SBA-16 material showed promising performance for application as active and stable catalyst in LT-WGSR.

During aging at higher temperature (350 °C), a more severe deactivation occurred, in agreement with the fact that a strong metal support interaction (SMSI) state is obtained in the materials. The loss of catalytic activity can be related with the electronic deactivation induced by reduced CeO_{2-x} and by encapsulation of Pt nanoparticles resulting from partial sintering of the material, in a similar manner to Pd@CeO_2/Si-Al_2O_3 catalysts.[41]

The catalysts prepared by deposition-precipitation are not active enough to allow their application in LT-WGSR, although they are not negatively affected by severe aging under WGSR. The lower activity derives from the less extension of Pt-CeO_2 interaction while the higher stability is obtained thanks to the higher dispersion/accessibility of the Pt component.

4. Conclusions

Nanocomposites materials with a Pt/CeO_2 active phase dispersed within highly porous silica with well-defined cubic symmetry of pore scaffold (SBA-16) have been prepared and tested as catalysts for the low temperature WGSR, an important industrial process involved in large scale production of pure H_2. Different synthetic methods have been compared with the final aim to maximize the interactions of Pt and CeO_2 nanocrystallites, yielding active and stable catalysts. The preparation methodology greatly affected the textural and morphological properties of the synthesized materials. The key to achieve more active and stable catalysts is the confinement of the active phase within the SBA-16 scaffold, and the enhancement of the interaction between Pt nanoparticles and CeO_2 nanocrystallites, as evidenced by H_2 chemisorption and catalytic tests. The catalytic WGSR performance was optimized in IMP materials by exploitation of the interactions of functionalized Pt-DT nanoparticles with cerium decyloxide and by the hydrophobization of the SBA-16 support.

5. Acknowledgments

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†Electronic Supplementary Information (ESI) available: details of the synthesis of Pt and CeO_2 precursors for impregnation method, typical SAED pattern and additional SEM characterization, additional catalytic tests and characterization of the catalyst after WGSR.

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Table 1. Textural properties of SBA-16 and nanocomposites materials obtained from N_2 physisorption data[a] and average crystallite size obtained from XRD using the Scherrer equation[b].

Sample	Surface Area[a] (m^2/g)	Pore Width[a] (nm)	Pore Volume[a] (cm^3/g)	CeO_2 Crystallite size[b] (nm)
SBA-16	747	6.5	0.49	-
DP_Pt/CeO_2(10%)/SBA-16	613	6.5	0.44	3±1
DP_Pt/CeO_2(20%)/SBA-16	773	6.5	0.49	3±1
IMP_Pt@CeO_2(10%)/SBA-16	434	7.4	0.54	2±1
IMP_Pt@CeO_2(20%)/SBA-16	306	7.5	0.43	3±1
IMP_Pt@CeO_2(10%)/H-SBA-16	549	6.5	0.35	4±1
IMP_Pt@CeO_2(20%)/H-SBA-16	304	6.4-7.1	0.28	3±1

Table 2. H_2 chemisorption results on the synthesized Pt-CeO_2/SBA-16 materials: H/Pt values measured at 35 °C and -90 °C and their ratio (R).

Sample	H/Pt at -90°C	H/Pt at 35°C	R
DP_Pt/CeO_2(10%)/SBA-16	0.743	1.084	1.46
DP_Pt/CeO_2(20%)/SBA-16	0.701	1.312	1.87
IMP_Pt@CeO_2(10%)/SBA-16	0.401	1.451	3.62
IMP_Pt@CeO_2(20%)/SBA-16	0.374	1.896	5.07
IMP_Pt@CeO_2(10%)/H-SBA-16	0.384	3.176	8.27
IMP_Pt@CeO_2(20%)/H-SBA-16	0.330	4.492	13.6

Table 3. Light-off temperature (T_{50}) and the temperature at which the chemical equilibrium for the WGSR is achieved (T_{EQ}) during light-off experiments after different aging treatments.

Sample	T_{50}			T_{EQ}		
	Fresh	Aging 350°C x 16h	Aging 350°C x 20h	Fresh	Aging 350°C x 16h	Aging 350°C x 20h
DP_Pt/CeO_2(10%)/SBA-16	258	237	239	294	262	265
DP_Pt/CeO_2(20%)/SBA-16	224	229	228	294	291	292
IMP_Pt@CeO_2(10%)/SBA-16	203	239	230	228	257	265
IMP_Pt@CeO_2(20%)/SBA-16	190	229	218	210	254	245
IMP_Pt@CeO_2(10%)/H-SBA-16	175	210	216	210	234	238
IMP_Pt@CeO_2(20%)/H-SBA-16	165	212	207	200	221	231

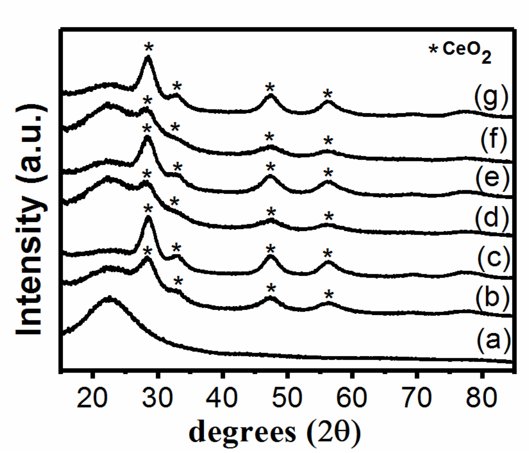

Fig. 1. Wide angle XRD patterns of SBA-16 (a), DP_Pt/CeO_2(10%)/SBA-16 (b), DP_Pt/CeO_2(20%)/SBA-16 (c), IMP_Pt@CeO_2(10%)/SBA-16 (d), IMP_Pt@CeO_2(20%)/SBA-16 (e), IMP_Pt@CeO_2(10%)/H-SBA-16 (f) and IMP_Pt@CeO_2(20%)/H-SBA-16 (g). The positions corresponding to the main reflections of the fluorite structure of CeO_2 are also shown.

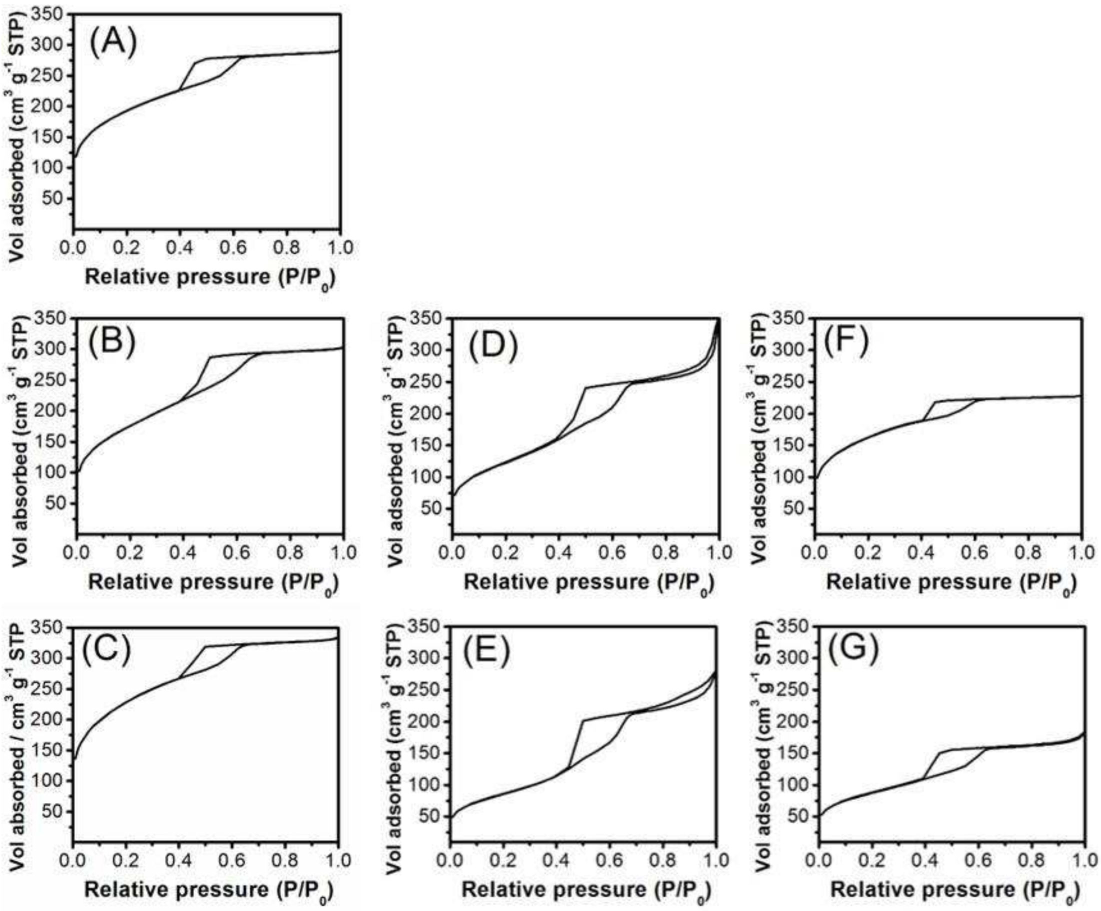

Fig. 2. N_2 physisorption isotherms collected at the liquid nitrogen temperature for SBA-16 (A), DP_Pt/CeO_2(10%)/SBA-16 (B), DP_Pt/CeO_2(20%)/SBA-16 (C), IMP_Pt@CeO_2(10%)/SBA-16 (D), IMP_Pt@CeO_2(20%)/SBA-16 (E), IMP_Pt@CeO_2(10%)/H-SBA-16 (F) and IMP_Pt@CeO_2(20%)/H-SBA-16 (G).

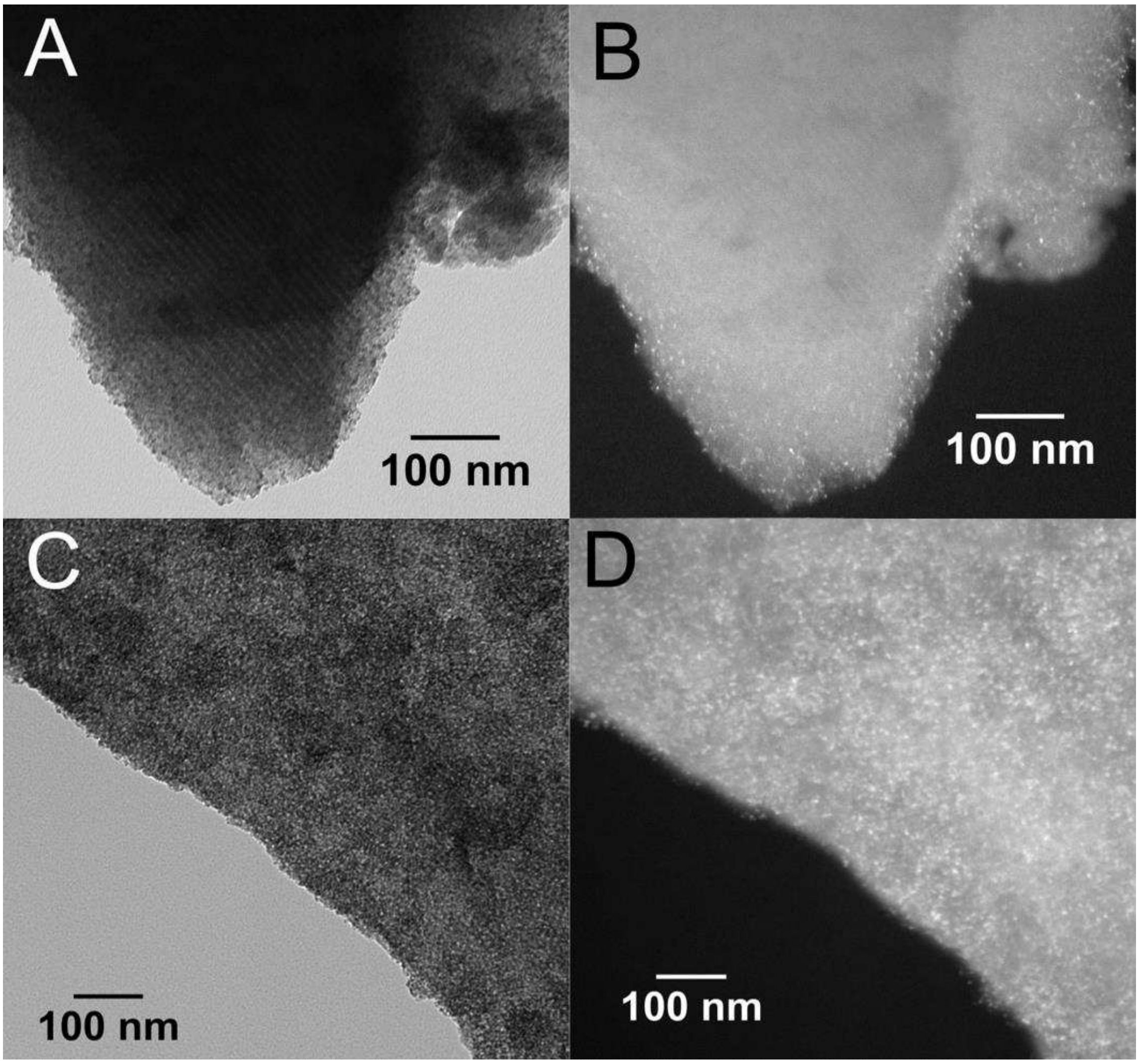

Fig. 3. Representative TEM images of DP_Pt/CeO_2(10%)/SBA-16 (A-B) and DP_Pt/CeO_2(20%)/SBA-16 (C-D). Bright field (A-C) and dark field (B-D).

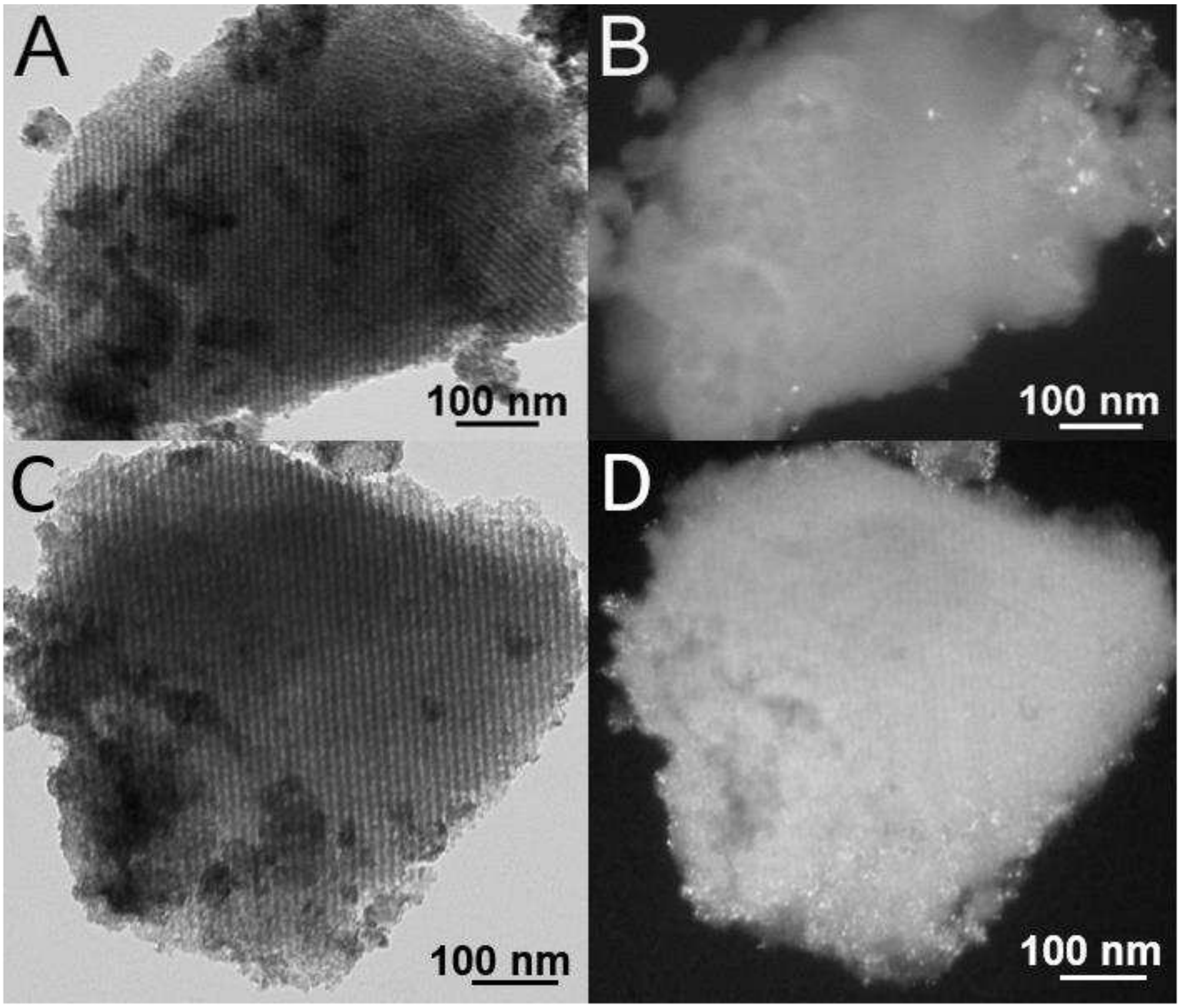

Fig. 4. Representative TEM images of IMP_Pt@CeO_2(10%)/SBA-16 (A-B) and IMP_Pt@CeO_2(20%)/SBA-16 (C-D). Bright field (A-C) and dark field (B-D).

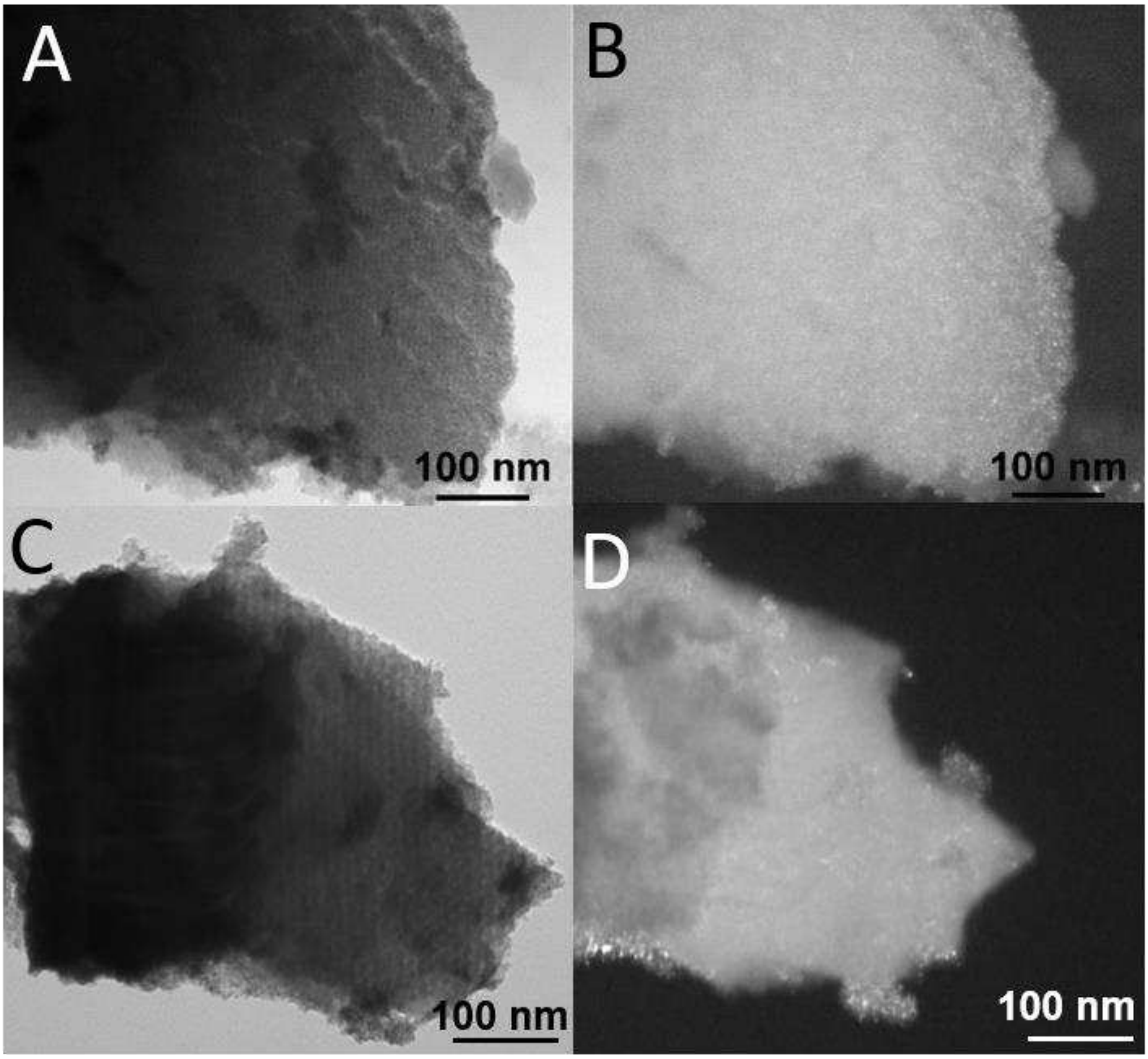

Fig. 5. Representative TEM images of IMP_Pt@CeO_2(10%)/H-SBA-16 (A-B) and IMP_Pt@CeO_2(20%)/H-SBA-16 (C-D). Bright field (A-C) and dark field (B-D).

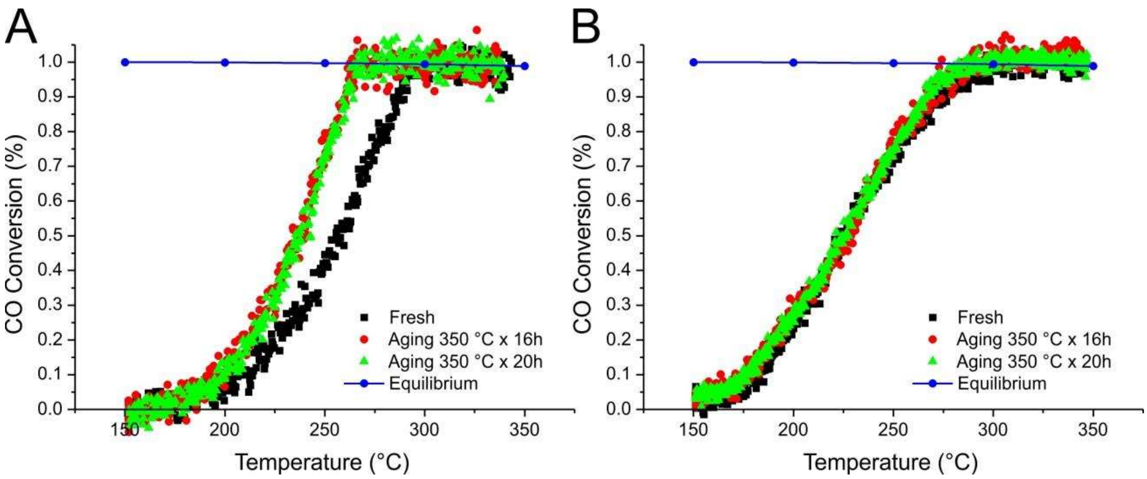

Fig. 6. CO conversion during WGSR over DP_Pt/CeO_2(10%)/SBA-16 (A) and DP_Pt/CeO_2(20%)/SBA-16 (B) catalysts.

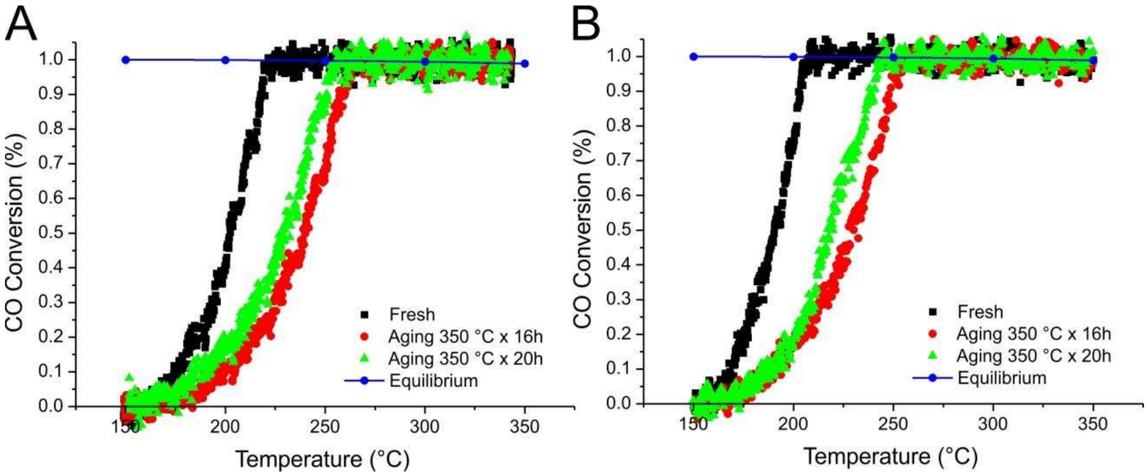

Fig. 7. CO conversion during WGSR over IMP_Pt@CeO_2(10%)/SBA-16 (A) and IMP_Pt@CeO_2(20%)/SBA-16 (B) catalysts.

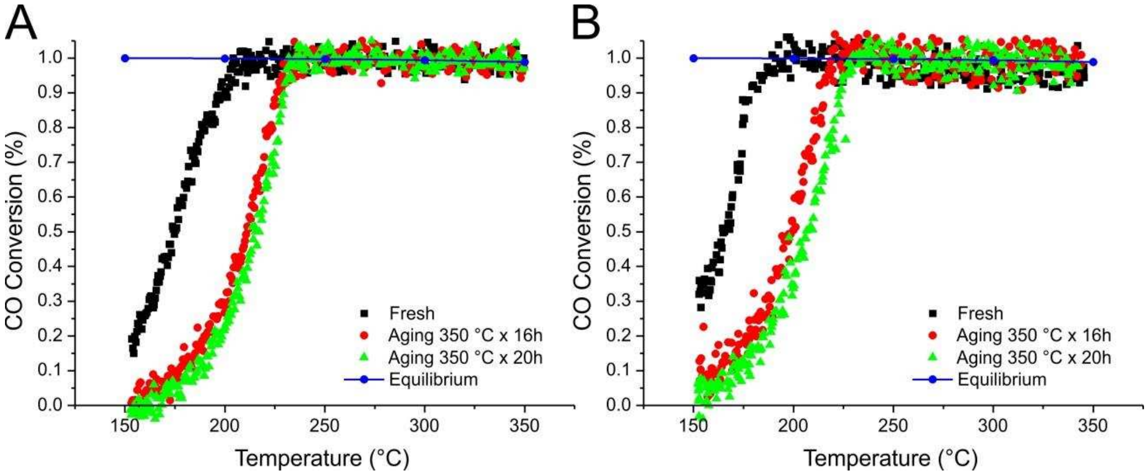

Fig. 8. CO conversion during WGSR over IMP_Pt@CeO_2(10%)/H-SBA-16 (A) and IMP_Pt@CeO_2(20%)/H-SBA-16 (B) catalysts.