

INVESTIGATION OF A Pt CONTAINING WASHCOAT ON SiC FOAM FOR HYDROGEN COMBUSTION APPLICATIONS

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Abstract

A commercial Pt based washcoat, used for catalytic methane combustion, was studied supported on a commercial SiC foam as catalytic material (Pt/SiC) for catalytic hydrogen combustion (CHC). Structural and chemical characterization was performed using Electron Microscopy, X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS). The reaction was monitored following water concentration by Fourier Transform Infrared spectra (FTIR). The FTIR method was compared with H₂ detection by Gas Chromatography (GC) and has shown to be adequate to study the kinetics of the CHC reaction in steady state under our experimental conditions (very

lean 1% (v/v) H₂/air mixtures). The catalyst is composed of 5-20 nm dispersed Pt nanoparticles decorating a mixture of high surface area Al₂O₃ and small amounts of ceria supported on the SiC foam which also contains alumina as binder. The Pt/SiC catalytic material has demonstrated to be active enough to start up the reaction in a few seconds at room temperature. The material has been able to convert at least 18.5 L_{hydrogen}·min⁻¹·g_{Pt}⁻¹ at room temperature in conditions of excess of catalyst. The Pt/SiC material was studied after use using XPS and no significant changes on Pt oxidation states were found. The material was characterized from a kinetic point of view. From the conversion-temperature plot a T₅₀ (temperature for 50% conversion) of 34 °C was obtained. Activation energy measured in our conditions was 35±1 kJ·mol⁻¹.

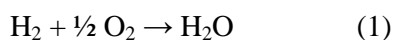
Keywords

Hydrogen, catalytic combustion, FTIR, Pt-washcoat, SiC ceramic foam

Introduction

There is a general consensus that global energy resources will face a growing demand in the next decades due to the increasing worldwide requirement of energy. Fossil fuel consumption, the most employed energy resource, produces carbon dioxide and other contaminants which contribute to greenhouse effect. For these reasons, the world should move to more sustainable energy resources. In this context, hydrogen appears as an attractive energy *carrier* with high energy density (142 MJ·kg⁻¹ while for liquid hydrocarbons is 47 MJ·kg⁻¹) and with the possibility to produce energy without the formation of carbon dioxide [1-3]. For the implementation of the “hydrogen economy” challenges related to production, transportation, storage and combustion should be met first. Catalytic hydrogen combustion (CHC, reaction (1)) is a key reaction in the

“hydrogen economy” which can be employed as a means of heat production (cookers, heaters, etc) as well as for safety purposes [4-17]:



Over the conventional hydrocarbon-based fuels employed for heating, hydrogen is advantageous because presents catalytic ignition at lower temperatures, the feasibility to adopt inexpensive oxide catalysts, and no generation of carbon-based residues [4-9]. Regarding safety, many papers report the use of CHC for the management of lean and/or explosive mixtures in a wide range of conditions and applications, from the destruction of residual hydrogen in the exhaust of fuel cells to the prevention of destructive explosions in nuclear reactors [10-17].

Reaction (1) is highly exothermic ($-286 \text{ kJ}\cdot\text{mol}^{-1}$) and can be controlled using appropriate catalysts, in contrast to flame combustion which produces NO_x and presents well-known safety issues such as flashback possibility [15, 18]. Regarding catalysts, the report by Haruta and Sano is the most complete in terms of catalyst screening and comparison [18]. Pt is a very well established catalyst and is one of the most active for CHC, capable of burning hydrogen through reaction (1) even at room temperature [4,5,7,9,11,12,15,16,18]. Thinking of a practical application for reaction (1), catalyst should be prepared in supported form, which improves dispersion, prevents aggregation and facilitates its use in successive cycles. Most papers report the use of metal oxides such as SiO_2 , TiO_2 , CeO_2 , SnO_2 , ZrO_2 , etc and other ceramics as catalyst support [7,14,17,19]. However, if CHC is thought to be employed for heating purposes, silicon carbide should be considered as a support of election due to its high mechanical strength, chemical inertness and high thermal conductivity to prevent the formation of hot spots [20]. SiC has been reported previously as a support for other catalytic

reactions such as methane (or methane/H₂ mixtures) combustion and Fischer-Tropsch reaction [20-25] but only recently for the CHC reaction [26, 27]. In these previous works [26, 27], carried out by the EMPA laboratory, a commercial Pt washcoat (supplied by INFRAGAS and usually employed for methane combustion) was supported on clay bound SiC foams and used, in monolith form, as CHC catalyst for the design and construction of a H₂ based cooker. This hydrogen burner operates with air-fuel equivalent ratios (λ) in the range 1.5-3.0 [26]. In the present work we present the study of this Pt washcoat on the clay bound SiC foam (Pt/SiC material) as catalyst for CHC for very lean (1% v/v) H₂/air mixtures (λ equal to 42). This mixture is safe, and its hydrogen concentration permits to conduct the (very exothermic) reaction under nearly isothermal conditions, essential to characterize the catalyst from a kinetic point of view. Structural and chemical studies were also carried out for a full characterization of the catalyst. Kinetic studies were conducted using a novel method to study this reaction under the selected conditions which consists of measuring water concentration by FTIR in the exhaust gas. The validations of this method by comparison with the one based on the hydrogen detection by GC was also investigated in this work.

2. Experimental Section

2.1. Support and catalyst selection and fabrication.

The catalytic material under study was designed thinking of a practical application for heating. For this reason, a commercial SiC monolith foam (VUKOPOR[®]S80 from LANIK with 80 ppi) was selected as support. The use of a monolithic support is essential for this type of application because provides a high heat dissipation path through an interconnected structure, preventing the formation of hot spots. The clay bounded SiC foam was manufactured by the replication technology, using a

polyurethane porous template impregnated with a ceramic slurry layer, followed by a firing step. Details about the microstructural and chemical characterization of the SiC foam are given in section 3.1.

This commercial SiC support was further washcoated by another company (INFRAGAS s.r.l.), employing the methodology developed to prepare their commercial catalysts for methane combustion, also based on the methods described in Ref. [28]. The washcoat is based on a Pt phase dispersed on a porous alumina layer with ceria additives. Along the text the material under study will be denoted as Pt/SiC for simplicity. The quantification of minor components for this material, according to the supplier and the ICP-AES (Inductively coupled plasma atomic emission spectroscopy) analysis, gave values of 0.27wt% Pt and 0.2wt% Ce. Details about the microstructural and chemical characterization of the complete Pt/SiC material are also given in section 3.1.

2.2. Support and catalyst characterization

SEM (Scanning Electron Microscopy) analyses were performed on the as prepared support and catalyst in a high resolution SEM-FEG microscope Hitachi S4800 operating at 5keV. The EDX detector (Bruker-X Flash-4010) allows the registration of individual elemental mapping. Quantification of EDX spectra was done with the Expirit 1.8 software from Bruker. For TEM (Transmission Electron Microscopy) studies, sample was ground into powder and then dispersed in ethanol by ultrasound and dropped on a copper grid. TEM measurements were performed on a Philips CM200 microscope with a point resolution of 2.4Å equipped with an EDX detector (EDAX DX-4). The Pt particle size distribution was evaluated from the TEM micrographs. The images were processed with image analysis software to identify the particles as well-defined dark

contrast areas which were then analyzed with the ImageJ software [29]. XRD (X-ray Diffraction) measurements were performed on powdery materials using the Cu K α radiation in a Siemens D5000 diffractometer in a Bragg-Brentano configuration in the 2 θ angle range of 40-80 degrees. The quantitative phase analysis was done with the software X'Pert Highscore Plus from PANalytica B.V. XPS (X-ray Photoelectron Spectroscopy) spectra were recorded in powder form with a Leybold Heraeus LH10 spectrometer using Al K α radiation with 40 eV pass energy at normal emission take off angle. The spectra were calibrated by setting the signal corresponding to Si(IV)-O in the Si 2p level at 103.5 eV, according to literature [30]. For comparison, the spectra were normalized to the same area. Surface area (BET) measurements were carried out with a Micromeritics Tristar II equipment. Pulse chemisorption measurements were performed on an AutoChem 2920 chemisorption analyzer from Micromeritics.

2.3. Catalytic tests

Catalytic tests were performed in a fixed bed stainless steel reactor connected to a FTIR spectrometer for the detection of the reaction product (water). Prior to each experiment, the reactor was loaded with a certain amount of supported catalyst in form of granules. Smashing into granules instead of use in monolithic form permits to dilute the catalytic materials with SiC (uncoated support, also in the form of granules) to tune the (very high) activity of Pt in order to achieve the kinetic regime. In this regime, essential to evaluate catalytic properties (activation energy, T₅₀, etc.), the heat released by the reaction would be negligible in the very lean H₂/air mixtures and thus the formation of hot spots should not be an issue here. For a full coverage of the reactor section 400mg of total granules were employed in each experiment.

Reactions were carried out with a feed mixture consisting of 1% v/v H₂ in air. This H₂ concentration ensures that even for 100% conversion (0.625 wt% of water in the exhaust gas), the water content is below the saturation concentration in air (1.5wt% at 20°C). Water was therefore detected as vapor into the exhaust gases by measuring the absorbance at 1652 cm⁻¹ (water bending). FTIR spectra were measured in a Bruker ALPHA FT-IR spectrometer as a function of time (as well as temperature) and from each spectrum the signal at 1652 cm⁻¹ was extracted (after background subtraction). The system was calibrated by measuring the absorbance of known water/air mixtures. Conversion was calculated by comparing the absorbance at 1653 cm⁻¹ at a certain time with the absorbance of a 1% vol H₂O/air mixture (0.066). The reactor was heated from outside using an electric furnace and temperature was controlled using a PID controller. Temperature was measured by a K-type thermocouple placed at the center of the packed bed. Kinetic experiments were performed with and without catalyst, to exclude the amount of water generated by the reactor itself, which is important at high temperatures. Catalyst was tested with no previous conditioning treatment.

The methodology of measuring water through FTIR measurements was validated by comparing with the well established GC method. For this purpose, a HP 5890 chromatograph was employed to measure H₂ amount, with a ShinCarbon packed column and a thermal conductivity detector. N₂ was used as a carrier gas. Those experiments in which conversion was measured by GC will be clearly mentioned in the text. When there is no mention of the methodology employed, readers must assume that FTIR is employed.

3. Results and Discussion

3.1. Characterization of the Pt washcoat on SiC

The microstructural and chemical characterization of the Pt/SiC catalytic material was considered first relevant for this study and for the interpretation of kinetic results. First of all, SiC foam support (before washcoating) was characterized by SEM. Results are supplied in Fig. 1a and as supporting information (Fig. S1). Figure 1a shows a low magnification SEM image which shows the highly porous structure of the SiC foam. Higher magnification SEM images (Fig. S1) show the surface texture with defined grains of various sizes. Al and Si elemental maps obtained by EDX (Fig. S1) permit to distinguish the presence of SiC (majoritary) and Al₂O₃ -containing particles. Alumina, respectively clay, is often used as binder for the fabrication of SiC foams. For this support a value of 5.3 was found for the Si/Al atomic ratio by quantification of EDX spectra obtained from general areas at low magnification.

The complete Pt/SiC material was then characterized by SEM (monolithic form) and TEM (powder form). A high magnification SEM image of a representative zone is shown in Fig. 1b. Figures 1c-f show the corresponding elemental maps. Al and Si maps show the presence of SiC and Al₂O₃ particles. Alumina particles may correspond to the binder of the SiC foam as well as to additional Al₂O₃ from the washcoat. Ce and Pt elemental maps indicate the presence of these elements decorating some porous-like alumina particles (indicated by arrows in Fig.1b), but the intrinsic resolution of this method does not permit to observe individual Pt particles. For the Pt/SiC material a value of 4.3 was found for the Si/Al atomic ratio by quantification of EDX data obtained from general areas at low magnification. This value indicates the additional amount of Al due to the supported porous-like alumina of the washcoat when compared to pure SiC foam (Si/Al atomic ratio of 5.3). TEM images with their corresponding EDX spectra (indicated by arrows) in Figure 2 reveal the presence of small and disperse Pt nanoparticles which are in the range of 5-20 nm (Table 1). The Pt nanoparticles

appear decorating a porous Al_2O_3 particle bound to SiC in Fig. 2a. A Ce-containing Pt decorated porous Al_2O_3 particle is shown in Fig. 2b. The identification of washcoat particles separated from the SiC support is due to sample preparation based on grinding the material into powder. The microstructure of the applied washcoat is therefore consisting of Pt nanoparticles dispersed on porous alumina with ceria additives. The Pt particle size distribution plot is found in Fig.2.d. (inset). The analysis of the plot shows a broad dispersion in the range 5-20 nm with an average particle size of 11 nm with a standard deviation of 4 nm.

Figure 3 shows the XRD study of the Pt/SiC catalytic material in comparison to the SiC support. The diffractogram of the foam support (curve a) is shown together with reference materials data (above) and indicates the presence of SiC (ICSD 01-072-0018), Al_2O_3 (ICSD 01-071-1124) and SiO_2 (00-077-1317), indicating a clay bonded SiC foam structure. The composition of the SiC foam support was determined by the quantitative phase analysis of X-Ray diffraction data giving 80% SiC, 8% Al_2O_3 and 12% SiO_2 . These values correspond to a Si/Al atomic ratio of 5.7 in agreement with the ratio determined by EDX. The Pt/SiC material (curve b) shows in addition the Pt peak at 39.76 degrees (2θ) assigned to (111) plane and some broad signals (indicated with dots) corresponding to CeO_2 (ICDD 01-078-0694). Platinum particle size was estimated using Scherrer's formula in the (111) Pt peak resulting in average size of 17 nm (Table 1), in consistence with TEM observations.

Surface electronic states of the fresh Pt/SiC supported catalyst were studied using XPS. Calibration of the spectra was done by setting the Si(IV)-O peak at 103.5 eV [30] according to XRD measurements (which showed the presence of SiO_2 as discussed above). Figure S2 in the supporting information shows the Si 2p and C1s XPS spectra. Figure 4a shows the Pt 4f together with Al 2p levels for the fresh Pt/SiC material in

comparison with the SiC support. The analysis of the Pt 4f peak is difficult because of superimposition with the more intense aluminium signal. By this reason the less intense Pt 4d peak was also registered and is presented in Fig. 4b. Although very noisy the position of the Pt 4d_{5/2} at 314.6 eV clearly indicates the presence of metallic Pt, the presence of small amounts of Pt(II) at 317.3 eV cannot be disregarded [31], The Al 2p peak can be assigned to a mixture of Al₂O₃ and surface AlOOH (75.69 and 74.9 eV respectively) according to Ref. [32]. The increase in the intensity of the Al 2p peak after the application of the washcoat to the SiC foam is originated on the high surface area of the alumina dispersing phase for the Pt particles in the washcoat. The study of the Si 2p together with C 1s level (Figure S2 supplied as supporting information) indicates the presence of Si-C and Si-O both in bare support and fresh catalytic material. The Ce 3d level (not shown) was not considered in this study because measured spectra were too weak and noisy to distinguish oxidation states.

Sorption experiments were also performed on the Pt/SiC material and bare SiC support. Nitrogen adsorption/desorption experiments show a negligible surface area and macroporous structure for the SiC foam as expected with a microstructure of 80 pores per inch as shown in Fig. 1a. The Pt/SiC catalytic material shows a 4.5 m².g⁻¹ surface area with a mesoporous structure characterized by a 13 nm pore diameter (Table 1). This increase in surface area and porosity is due to the application of the washcoat. Hydrogen chemisorption was also performed on the 0.27 wt% Pt/SiC supported catalyst giving a 8.5 % metal dispersion (assuming one atom of hydrogen chemisorbed on one exposed metal atom) [33]. Metal surface area was 21m².g_{metal}⁻¹ and the active particle diameter was 13.4 nm, in accordance to TEM and XRD particle size measurements (as shown in Table 1). Metal dispersion is not very high (only 8.5%) and should be improved in further works. However, washcoating has demonstrated to be an efficient

strategy to decrease particle size and improve dispersion, for such a hydrophobic support as SiC. Our first attempts (results not shown) to disperse Pt on bare SiC were unsuccessful, obtaining big and aggregated particles, owing to low metal-support interactions. The washcoating approach on SiC was reported before for TiO₂ based washcoat employed on the Fischer-Tropsh reaction [34].

3.2. Catalytic experiments

The Pt/SiC catalytic material was characterized from a kinetic point of view. Selected test conditions (H₂ concentration, mixture flow rate) are typical for catalyst comparison under nearly isothermal conditions [18]. However, because of the high activity of Pt, to achieve the kinetic regime a series of experiments were conducted first (as it will be described in the next section) to optimize catalyst amount and reduce the percentage of conversion. The kinetics of CHC was monitored by measuring the absorbance of the exhaust gas at 1653 cm⁻¹ which corresponds to water bending frequency. Even in conditions of 100% conversion, the water vapor concentration is below the saturation point of water in air (Fig. S3). The plot of absorbance as a function of water concentration (calibration curve) is supplied in the same figure as supporting information. Experiments in absence of catalyst are shown in Fig S4.

3.2.1. Experiments under high conversion conditions

CHC was first studied at different temperatures (30, 45, 92 and 420 °C) using a 200 ml.min⁻¹ flow of 1% v/v H₂/air mixture and 400 mg of catalyst. Figures 5.a and 5.b show the plot of absorbance at 1653 cm⁻¹ as a function of time in these conditions. Water signal reaches a steady state after a period of 20-30 min. The calculation of conversion in the regime of constant H₂O signal shows that, except for 30 °C (90% conversion) a 100 % conversion (0.066 absorbance units) was achieved in these

conditions. With a reduced mass of catalyst of 200 mg, using a flow of $1000 \text{ ml}\cdot\text{min}^{-1}$ for the 1% H_2 /air mixture, a 100 % conversion (at least $18.5 \text{ L}_{\text{H}_2}\cdot\text{min}^{-1}\cdot\text{g}_{\text{catalyst}}^{-1}$) was obtained in steady state starting the reaction at room temperature (kinetics not shown).

For a better comprehension of the results, same experiments were performed but in this case, the kinetics was monitored following the H_2 signal by GC and compared with the data following the water signal by FTIR. Figure 5.b and 5.c. show that using GC, the steady state in conversion is achieved and detected after a few minutes (5') while through FTIR, the steady state of the reaction is detected after longer time (25-30'). Water detection in the exhaust gas requires a stabilization time because of its intrinsic capability of adsorption on surfaces, including catalyst surface. However, once this stabilization period is finished, both GC and FTIR give similar results within the experimental error. This means, that FTIR is a reliable method to follow CHC on condition that stabilization period is achieved. Under steady-state conditions it permits to obtain information from the reaction (conversion) more frequently than GC because measurement is almost instantaneous and does not require elution time. It is important to mention here that the FTIR set up would be used in this paper alternatively or complementary with GC for the study of lean H_2 /air feed mixtures, below water saturation point.

The conversion vs. temperature curve for the Pt/SiC material was measured in cooling mode (from $420 \text{ }^\circ\text{C}$ to RT). The experiment was conducted using 400 mg catalyst and $200 \text{ ml}\cdot\text{min}^{-1}$ of 1% v/v H_2 /air mixture flow. The reactor temperature was first set at $420 \text{ }^\circ\text{C}$ and was then left to cool to room temperature overnight. Conversion (FTIR) and temperature were monitored during the experiment and results are shown in Figure 6. It is generally known that for homogeneous catalytic reactions, the kinetics follows a sigmoidal dependence of conversion on the temperature [16]. At lower temperatures

there is an exponential increase (fully in kinetic regime) followed by a higher temperature saturation regime (indicative of diffusional control) [16]. In our case, only the higher asymptote region of the sigmoidal curve can be observed, indicating a very high activity for the Pt/SiC catalyst in these conditions. The vertical region of the zone around room temperature does not permit to determine the temperature in which 50% conversion is achieved (T_{50}), because the error would be of the same order of magnitude of the value itself. For this reason, in subsequent experiments, catalyst amount was reduced to achieve the kinetic regime. After cooling, catalyst was studied by XPS. Figure 4.a and 4.b show the Pt 4f and 4d levels for the used catalyst in comparison to the fresh one. As already mentioned, the Pt 4f level is superimposed to the high intensity Al 2p signal, but the comparison of the (noisy) Pt 4d level (Fig.4.b) before and after use permits to conclude that electronic states of Pt remained unchanged as suggested in Fig. 4a and has been determined mainly as metallic Pt . As mentioned above, the detailed study of Ce 3d could not be performed because of bad quality of spectra due to its small quantity and low dispersion. However, metal support effects as reported before cannot be completely disregarded and the ceria additive is most probably favoring the kinetics of the reaction [15].

3.2.2. Experiments in kinetic regime

For a full characterization of the Pt washcoat from a catalytic point of view, a series of experiments were conducted in the kinetic regime. To achieve these conditions, the catalyst amount was reduced to 50 mg. The conversion vs temperature curve, measured at a $200\text{ml}\cdot\text{min}^{-1}$ 1% v/v H_2 /air flow (in heating mode) is presented in Fig. 7.a. and shows a T_{50} (temperature for 50% conversion) of 34°C . It is generally accepted that T_{50} is a parameter to compare activity between catalysts, but in the field of CHC is hard to find in literature catalysts tested under strictly the same conditions that herein presented.

However, though tested under different conditions (but still in excess of oxygen), the T_{50} obtained in this work is similar to that reported for other Pt-based catalysts such as PtO_2 and Pt-substituted oxides (claimed to be more active than those Pt-impregnated) which range from 25 to 40°C [15,16,18].

Reaction kinetics was also tested at different temperatures (24, 28, 33, 41.5 and 50 °C) and also different flow rates (150, 200 and 300 ml.min⁻¹) in steady state. Results are shown in Table 2. At 24 °C, the increase in flow rate from 150 to 300 ml.min⁻¹ produces a decrease in conversion from 38 to 24%. This behavior is predictable for a catalytic reaction in the kinetic regime. The Arrhenius plot (at 200ml.min⁻¹ 1% v/v H₂/air) is found in Figure 7.b and 35kJ.mol⁻¹ activation energy was obtained from the slope for the Pt/SiC material. Early works on CHC on Pt surfaces (Pt wire) claim that in large excess of oxygen (as herein), two distinct stationary-state catalysts were obtained: one of high activity when decreasing temperature and another of lower activity when the catalyst is raised from a low to a higher temperature [19]. Previous reports for Pt/SiO₂ and Pt wire obtained 7.5 and 10kJ.mol⁻¹ activation energies (respectively) from the conversion vs temperature experiments in cooling mode (from high to low temperature) [19]. Those conditions (cooling) permit to catch the high activity steady state surface of catalysts while our conditions caught the less active surface by raising temperature from RT to higher [19]. Under raising temperature conditions, as herein presented, Boreskov et al obtained for the same Pt wire catalyst an activation energy of 33kJ.mol⁻¹, very similar to our Pt/SiC material [19].

Thinking of the application for heating purposes, durability upon cycling was studied at 420 °C during 5 cycles of 1h feeding the reactor with 200ml.min⁻¹ 1% v/v H₂/air mixture. Results are presented in Fig. 8 and show high performance (100% conversion) and stability along successive cycles at high temperature.

4. Conclusions

A commercial 0.27 wt% Pt/SiC catalyst, employed previously by the EMPA laboratory for the design of a cooker based on catalytic hydrogen combustion, was characterized from a chemical, structural and catalytic point of view. SiC was selected as catalyst support because its high thermal conductivity is appropriate for the design of heating devices. To our knowledge, the use of this kind of support was not reported before for this reaction. The Pt washcoat catalyst is composed of 5-20 nm disperse (8.5% dispersion obtained by H₂ chemisorption) Pt nanoparticles supported on porous Al₂O₃ particles with some ceria additive. The washcoat is applied onto a clay bound SiC foam showing also alumina as binder and the SiO₂ phase. The catalyst has shown to be active enough to start-up the CHC at room temperature in all the conditions tested. The experimental set up, based on measuring water concentration (by FT infrared spectroscopy) in the exhaust gas, has demonstrated, once achieved the stabilization period, to be adequate to monitor the reaction producing similar steady state results to H₂ detection by gas chromatography for the study of lean 1% v/v H₂/air mixtures (typical for catalysts' testing). Experiments conducted under diffusional conditions have shown that the catalyst is able to convert at least 18.5 L_{hydrogen}·min⁻¹·g_{Pt}⁻¹ at room temperature. XPS experiments conducted on used catalyst has shown no significant change in Pt surface states (metallic platinum) in comparison to the fresh one. The T₅₀ (temperature of 50% conversion) obtained for the Pt/SiC washcoat was 34 °C. It is in the range of previously reported Pt based – catalysts and the measured activation energy was 35kJ·mol⁻¹. This work is a first approach to the use of SiC as catalyst support for CHC reaction and highlights the advantages of washcoating process to produce disperse nanoparticles on such a hydrophobic support. However, further work could be done to improve particle dispersion.

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References

- [1] Andreas Züttel, Andreas Borgschulte and Louis Schlapbach in “Hydrogen as a Future Energy Carrier”. Wiley-VCH, 2008.
- [2] Louis Schlapbach, Andreas Züttel, *Nature*, 414 (2001), 353-358.
- [3] John O'.M. Bockris, *Int. J. Hydrogen Energy*, 38 (2013) 2579-2588.
- [4] M. Haruta, Y. Souma, H. Sano, *Int. J. Hydrogen Energy*, 7 (1982) 729-736.
- [5] I. Wierzba, A. Depiak, *Int. J. Hydrogen Energy*, 29 (2004) 1303-1307.
- [6] M. Al-Garni, *Int. J. Hydrogen Energy*, 22 (1997) 383-387.
- [7] W. Choi, S. Kwon, H.D. Shin, *Int. J. Hydrogen Energy*, 33 (2008) 2400-2408.
- [8] M. Haruta, H. Sano, *Int. J. Hydrogen Energy*, 7 (1982) 737-740.
- [9] M. Haruta, H. Sano, *Int. J. Hydrogen Energy*, 7 (1982) 801-807.
- [10] K. Ledjeff, M. Haruta, H. Sano, *Int. J. Hydrogen Energy*, 12 (1986) 361-367.
- [11] F. Morfin, J-C Sabroux, A. Renouprez, *Applied Catalysis B: Environmental* 47 (2004) 47–58.
- [12] K.K. Sanap, S. Varma, S.B. Waghmode , S.R. Bharadwaj, *Int. J. Hydrogen Energy* 39 (2014) 15142- 15155.
- [13] N. Meynet, A.Bentaïb, V. Giovangigli, *Combustion and Flame* 161 (2014) 2192–2202.
- [14] C. Zhang , J. Zhang , J. Ma, *Int. J. Hydrogen Energy* 37 (2012) 12941- 12946.
- [15] P.A. Deshpande, G. Madras, *Applied Catalysis B: Environmental* 100 (2010) 481–490.
- [16] P.A. Deshpande, G. Madras, *Phys. Chem. Chem. Phys*, 13 (2011) 708–718.
- [17] V.M. Shinde, G. Madras, *Catalysis Today*, 198 (2012) 270-279.
- [18] M. Haruta, H. Sano, *Int. J. Hydrogen Energy*, 6 (1981) 601-608.
- [19] F.V. Hanson, M. Boudart, *Journal of Catalysis*, 53, 56-67, (1978), 56-57.

- [20] P. Marín, S. Ordóñez, F.V. Díez, *J. Chem. Technol. Biotechnol.*, 87 (2012) 360-367.
- [21] X. Guo, P.Brault, G. Zhi, A.Caillard, G. Jin and X. Guo, *J. Phys. Chem. C* 115, 2011, 24164–24171.
- [22] P. Leroi, B. Madani, C. Pham-Huu, M.J. Ledoux, S. Savin-Poncet, J.L. Bousquet. *Catalysis Today* 91–92 (2004) 53–58.
- [23] B. de Tymowski, Y.Liu, C.Meny, C. Lefèvre, D. Begin, P. Nguyen, C. Pham, D. Edouard, F. Luck, C. Pham-Huu, *Applied Catalysis A: General* 419– 420 (2012) 31–40.
- [24] S.Specchia, S. Tacchino, V. Specchia, *Chemical Engineering Journal* 167 (2011) 622–633.
- [25] S. Tacchino, L. D. Vella, S. Specchia, *Catalysis Today* 157 (2010) 440–445.
- [26] Patent pending: Vogt U., Fumey B., Biemann M., Züttel A.; Catalytic Hydrogenation Burner Setup. Empa Eidgenössische Materialprüfungs- und Forschungsanstalt. Patent No WO 2014/111427 A1, 15.01.2014
- [27] U. F. Vogt, B. Fumey, M. Biemann, V. Siong, N. Gallandat, A. Züttel, Catalytic Hydrogen Combustion on Porous SiC Ceramics, European Fuel Cell Forum 2011, 28 June -1 July 2011, Lucerne Switzerland, Fuel Cell Applications II, Chapter 15, Session B07 pp 45-54
- [28] H. Klein, J. Leyrer, R. Domesle, E. Lox, T. Kreuzer; Verfahren zur Herstellung einer beschichteten Katalysators. Degussa Aktiengesellschaft. Patent EP0920913A1, 13.11.1998
- [29] W. S. Rasband, ImageJ, U.S.N.I.o.H., Bethesda, Maryland, USA, imagej.nih.gov/ij/, 1997–2012
- [30] D.J.Park, Y. I. Jung, H. G. Kim, J. Y.Park, Y.H. Koo, *Corrosion Science*, 88, (2014) 416-422.

[31] i) A. M. Venezia, D. Duca, M. A. Floriano and G. Deganello, A. Royi, *Surface and Interface Analysis*, 19, (1992) 543-547. ii) J. Escard, B. Pontvianne, M.T Chenebaux, J Cosyns, *Bull. Soc. Chim. Fr.* 2400 (1975). iii) G. Schoen, *J. Electron Spectrosc. Relat. Phenom.* 1, 377 (1972).

[32] A. Bouifoulen, M. Edely, A. Kassiba, M. Makowska-Janusik, A. Outzourhit, J. Szade, A. Ouriagli, *Physica B* 406 (2011) 4500-4504.

[33] C.E. Hunt, *Journal of Catalysis*, 23, (1971) 93-96

[34] Y. Liu, I. Florea, O. Ersen, C. Pham-Huu, C. Meny, *Chem. Commun.*, 51, (2015) 145-148.

Figure captions

Figure 1.- SEM study on the Pt/SiC catalytic material. (a) General SEM micrograph showing the structure of the SiC foam. (b) Higher magnification SEM micrograph showing the structure of the Pt/SiC sample. (c)-(f) Elemental maps obtained from the area shown in (b): (c) Si, (d) Al, (e) Ce, and (f) Pt.

Figure 2.- TEM study of the Pt/SiC supported catalyst. (a) and (d) TEM micrographs of the catalyst. (b), (c), and (e) EDX spectra corresponding to the grains indicated by arrows in the micrographs. The inset in (d) corresponds to Pt particle size distribution as measured from several representative micrographs.

Figure 3.- Powder XRD of the Pt/SiC catalyst (a) along with the SiC foam support (b). Top-side: main diffraction peaks of reference materials (SiO_2 , Al_2O_3 and SiC). The CeO_2 peaks are indicated by dots.

Figure 4. XPS measurements on the fresh and used Pt/SiC material in comparison to the SiC foam support. (a) Al 2p + Pt 4f signals and (b) Pt 4d signal.

Figure 5. Kinetic experiments in high conversion conditions at constant 1% v/v H_2 /air mixture (flow rate, $200\text{ml}\cdot\text{min}^{-1}$) at different temperatures. Experiments were done by switching to a pure N_2 flow to recover signal background during reactor temperature changes. Curves (a) and (b) obtained by following the water signal using FTIR. Curves (c) and (d) obtained by following the reaction using both GC (H_2 signal) and FTIR (water signal).

Figure 6. Conversion as a function of temperature for the Pt/SiC material as catalyst for the H_2 combustion reaction under diffusional regime in cooling mode.

Figure 7. (a) Conversion as a function of temperature in heating mode for the Pt/SiC material as catalyst for the H₂ combustion reaction. (b) Arrhenius plot.

Figure 8. Durability of the Pt/SiC catalytic material upon cycling. Conversion as a function of cycle number at 420 °C.

Table Legends

Table 1: Characterization of the Pt/SiC catalytic material

Table 2. Conversion as a function of temperature and H₂ / air mixture flow rate for the experiments performed under kinetic control.

Table 1: Characterization of the Pt/SiC catalytic material

N ₂ sorption experiments		Hydrogen Chemisorption analysis			TEM	XRD
BET Surface area	Pore width	Metal dispersion	Metallic Surface area	Active particle diameter	Particle size	Particle size
4.5m ² .g ⁻¹	13nm	8.5 %	21m ² .g _{metal} ⁻¹	13.4nm	11 nm (average)	17 nm

Table 2. Conversion as a function of temperature and H₂ / air mixture flow rate for the experiments performed under kinetic control.

Flow rate (ml.min ⁻¹)	Temperature				
	24 (°C)	28(°C)	33(°C)	41.5(°C)	50(°C)
150	38	--	--	--	95
200	29	36	48	62	95
300	24	--	59	--	98

Figure 1

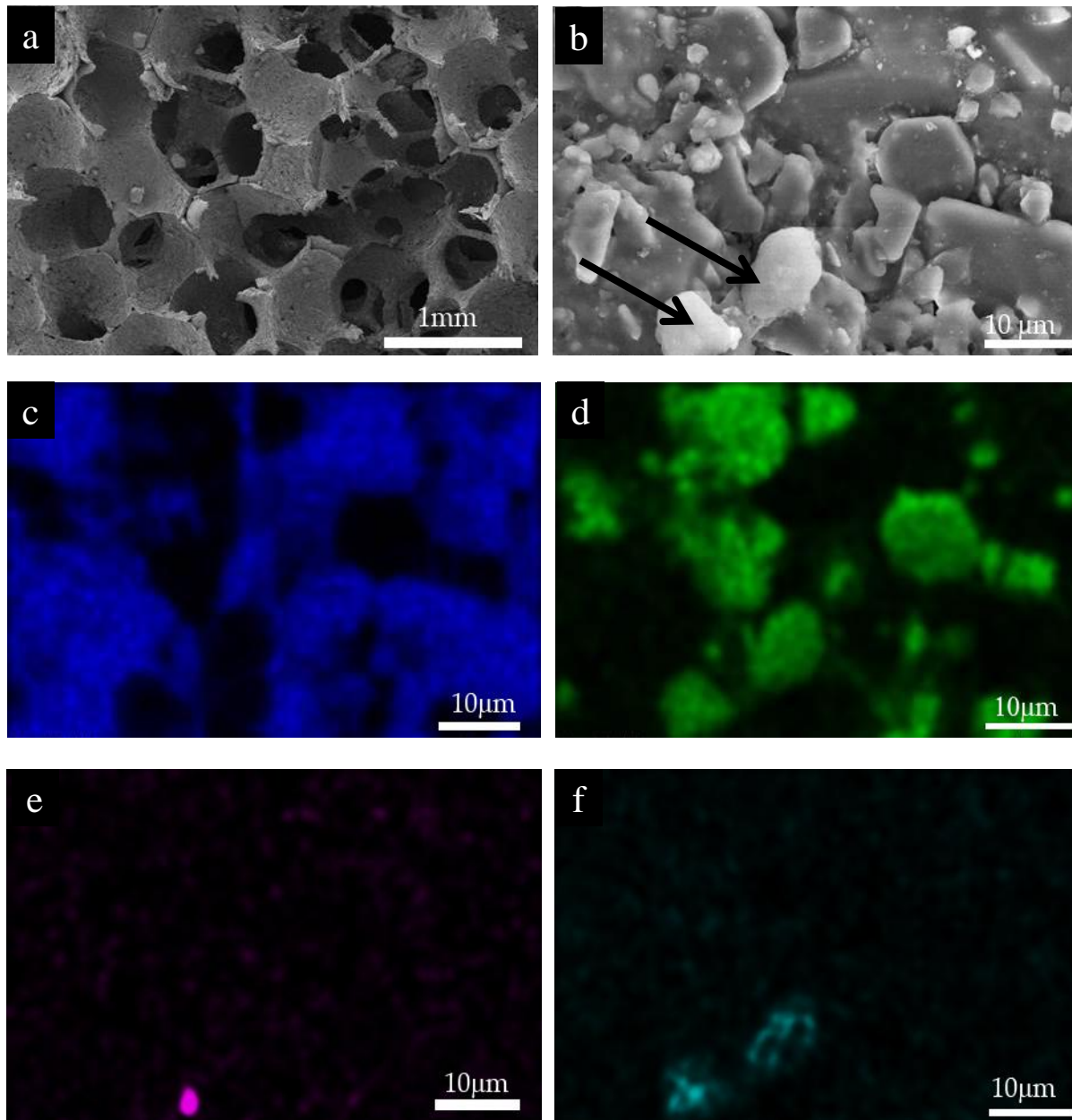


Figure 1

Figure 2 revised
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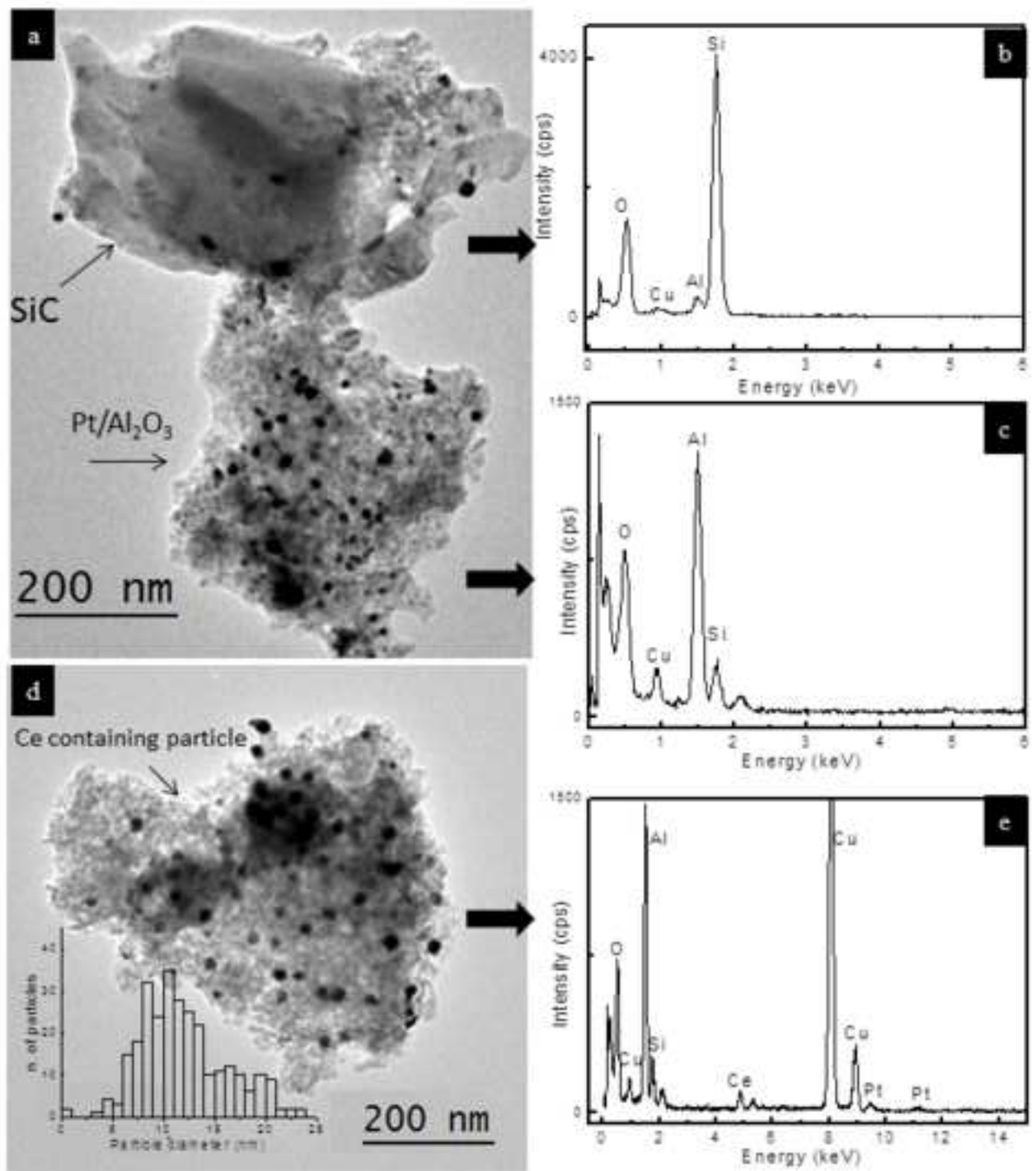


Figure 2.

Figure 3

Figure 3

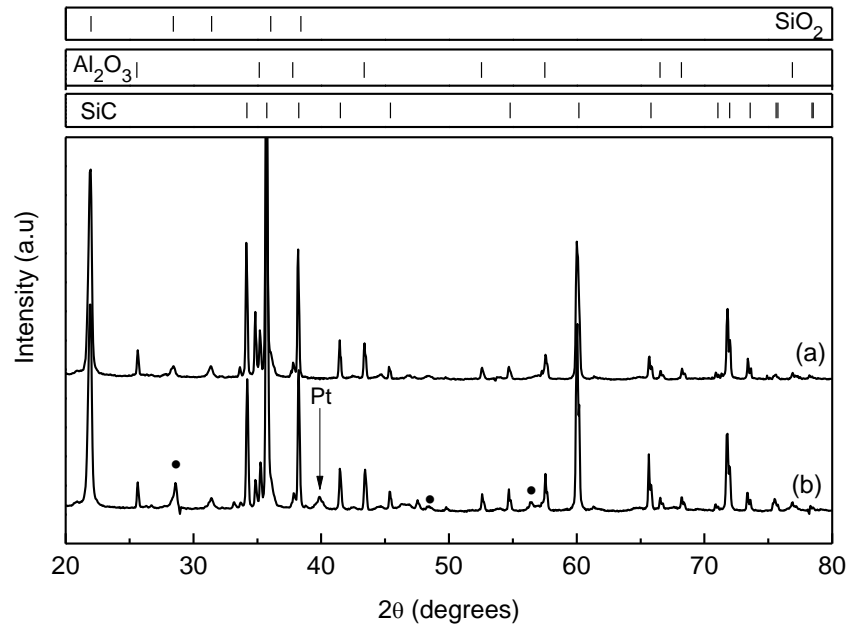
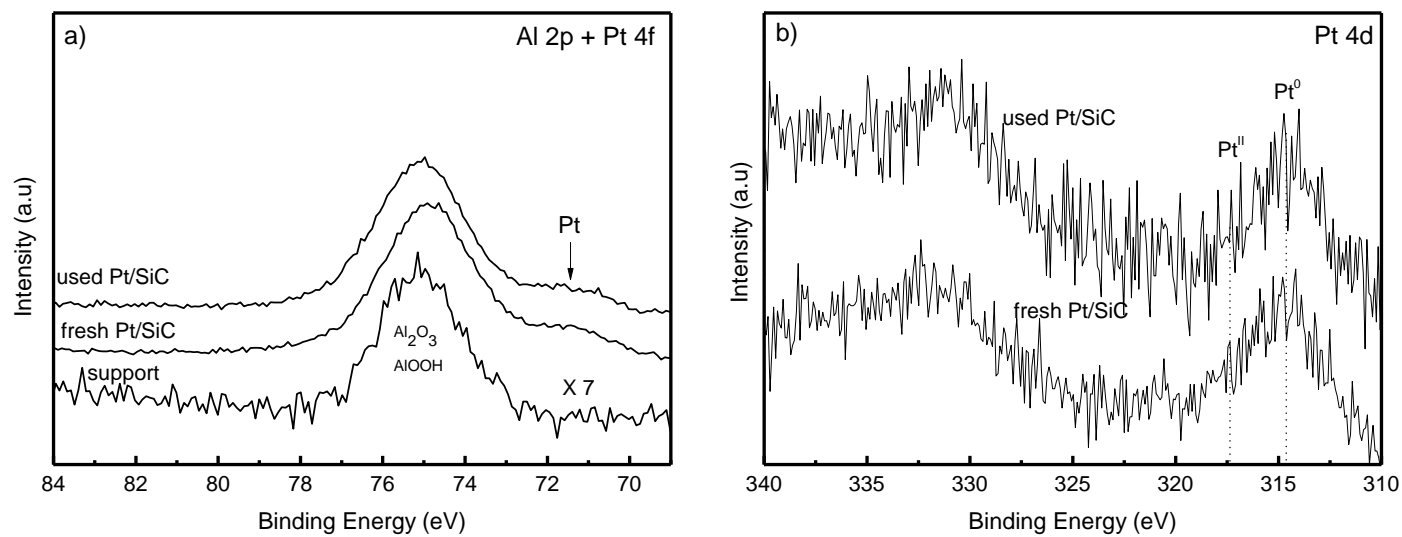


Figure 4



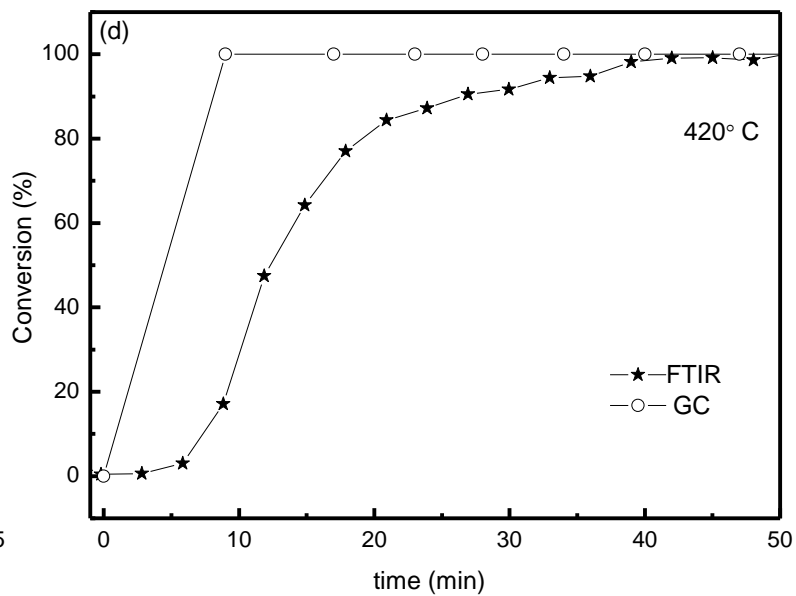
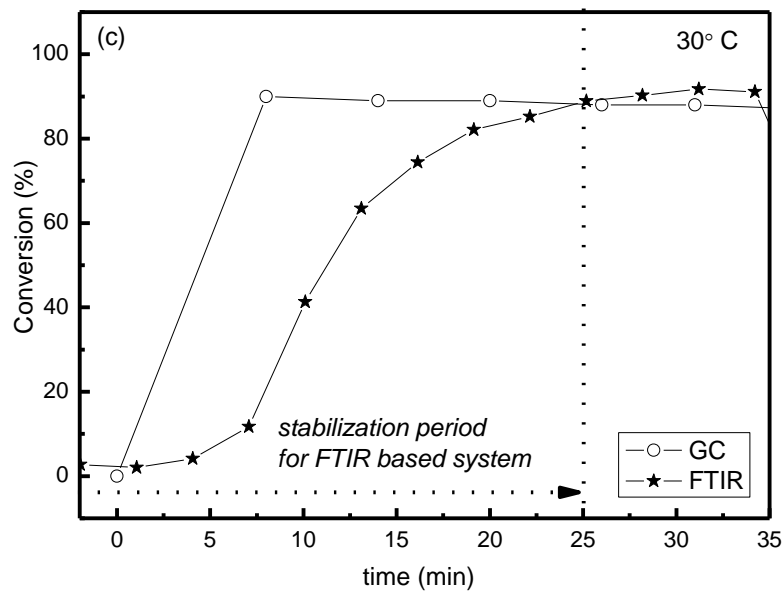
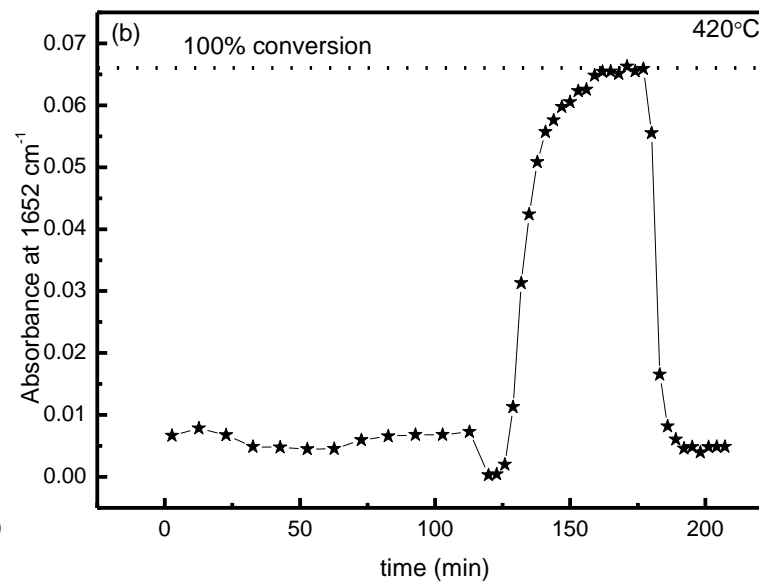
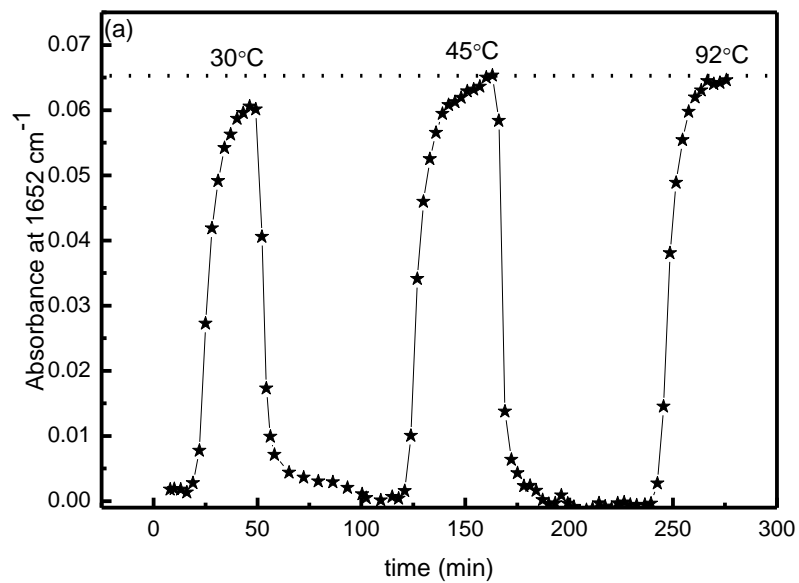


Figure 6

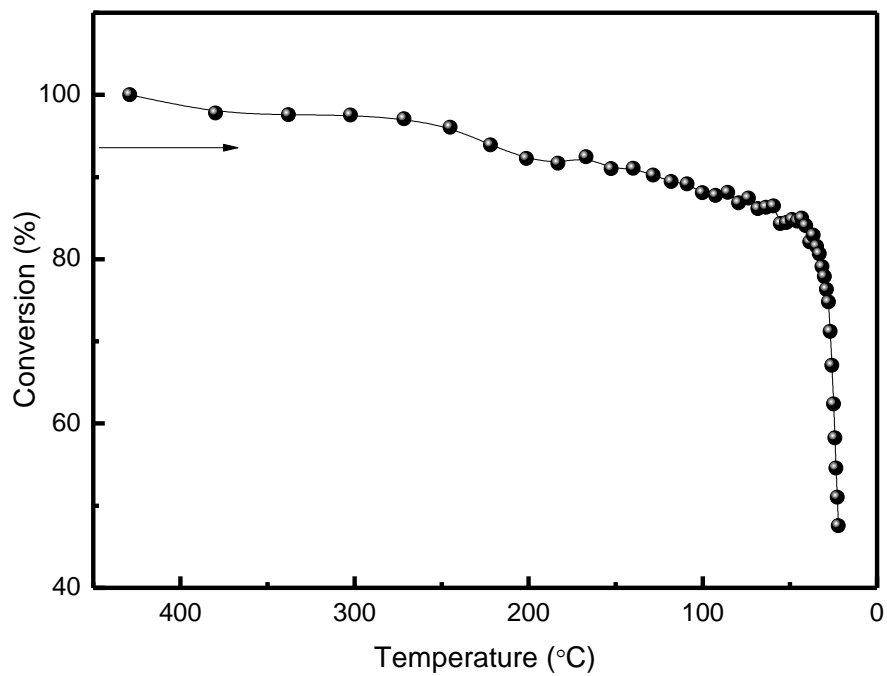


Figure 7

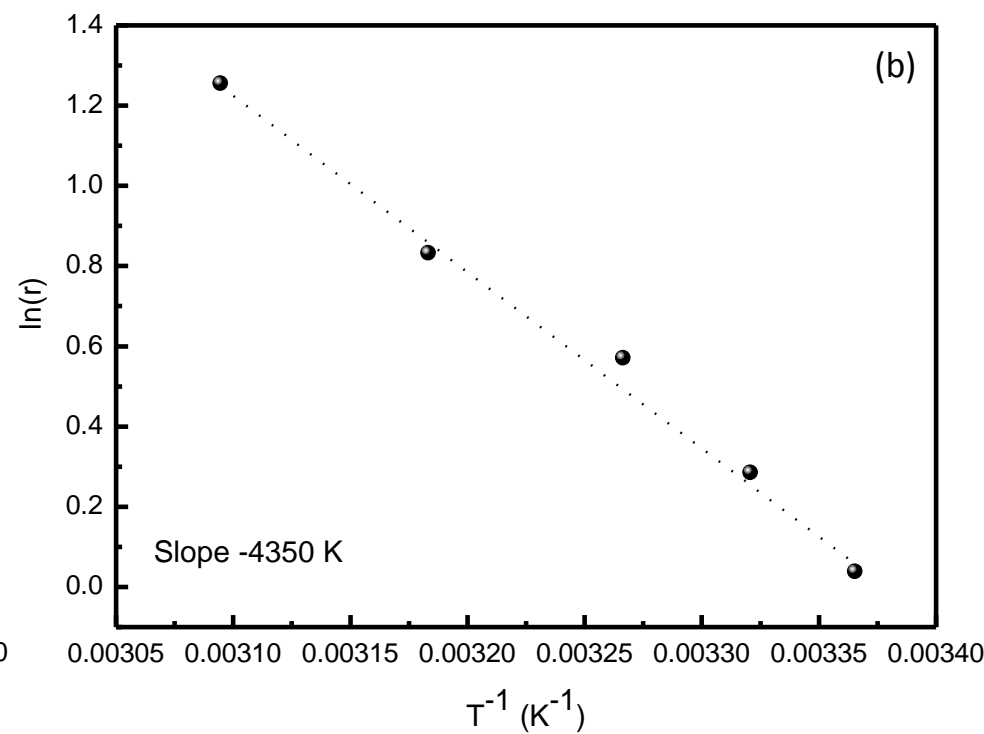
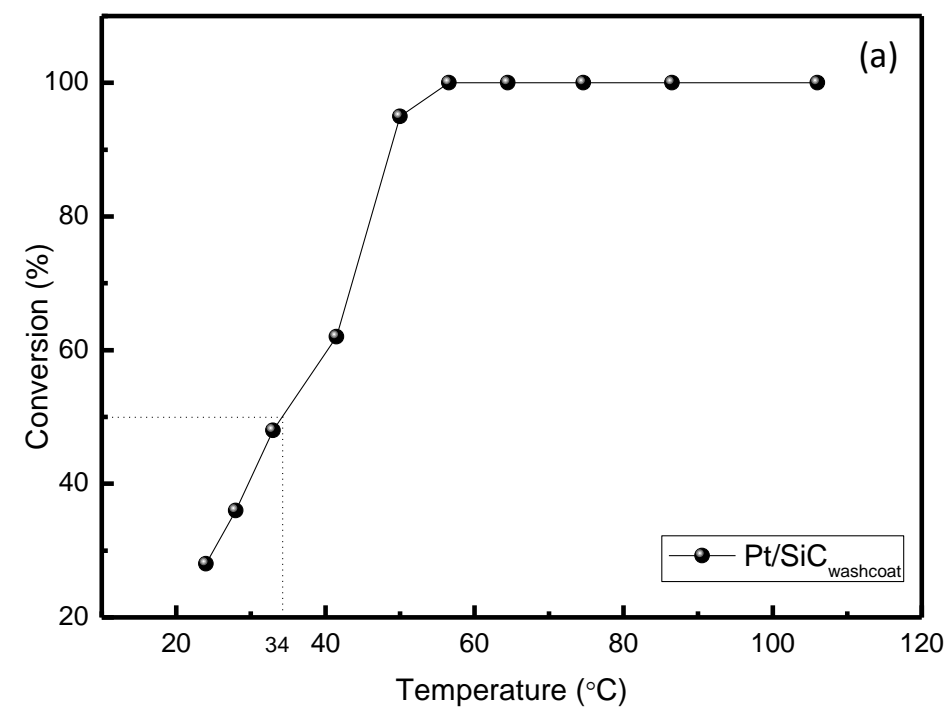
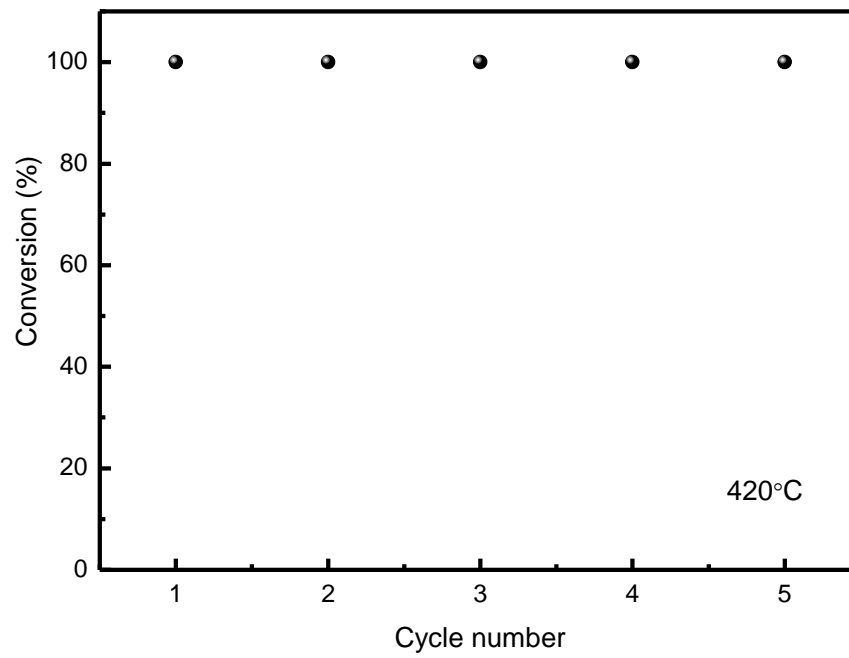
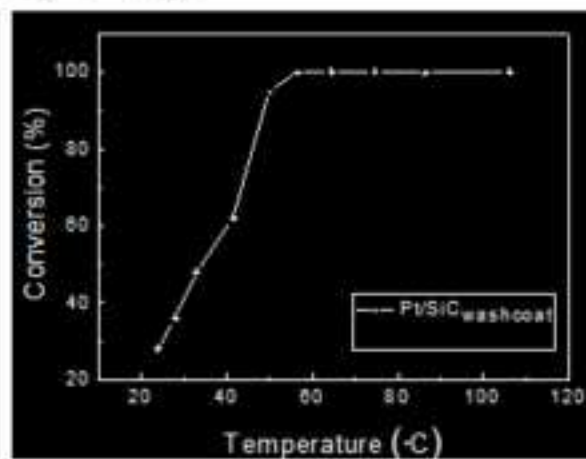
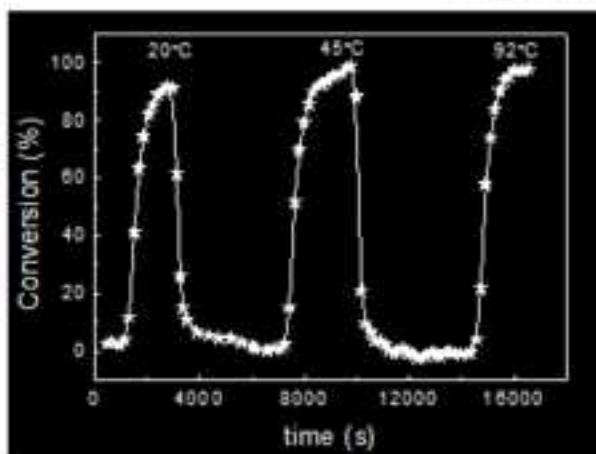
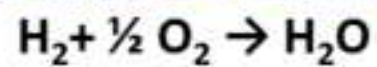


Figure 8



Pt based washcoat on SiC foam



Highlights

- Catalytic hydrogen combustion was studied in a Pt washcoat on SiC foam
- The catalyst contains Pt particles of 5-20 nm size on porous Al₂O₃ with ceria additive
- Kinetics was monitored by measuring water concentration through FTIR
- The Pt/SiC material shows high thermal stability and reaction start-up at room temperature
- Catalyst converted at least 18.5 L_{H₂}.min⁻¹.g_{Pt}⁻¹ with 35kJ.mol⁻¹ activation energy