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Effect of milling and doping on decomposition of NH_3BH_3 complex

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Abstract

The thermal decomposition of borane–ammonia complex as well as of milled and doped samples was studied by volumetric titrations. The samples were heated at fixed temperature and the volume of the evolved gas recorded as a function of time. Milled and doped samples were prepared by mechanical and mechanochemical reactions, respectively. Samples containing 1 and 2 mol% hydrogen hexachloroplatinate hydrate were prepared. The materials were characterized by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Mechanical alloying was effective to modify the crystallinity of the complex and to change the material morphology enhancing the amount of gas evolved. Both the milled and the doped samples showed an increase of the pre-exponential factor in the Arrhenius equation. The activation energy decreased for the doped sample, and it increased for the milled sample. As a result it was found that the decomposition of 1 mol% doped sample could be provided by waste heat coming from polymer electrolyte membrane fuel cell.

Keywords: Borane–ammonia; Ball milling; Hydrogen storage; Platinum; Activation energy

1. Introduction

The "hydrogen on demand" concept has been extensively publicized [1]. The system is a source of hydrogen with widely variable gas output flow rate and delivery pressure. Hydrogen is stored in hydrogen-rich material such us lightweight metal hydride ($NaBH_4$) dissolved in alkaline water. The material is storable in plastic containers at room temperature and without pressurization. Fuel and by-product are environmentally benign, non-flammable, and non-explosive. Hydrogen is released by action of a platinum or other precious metals-based catalyst on the fuel. The low cost and the simple hydrogen generation mechanism associated with high energy storage density, makes this concept extremely attractive for mobile applications.

Another possibility to generate hydrogen on demand is the thermal decomposition of materials with low decomposition temperature. Borane–ammonia (BA) complex is a very rich hydrogen compound (about 20% in mass) prepared in 1956 by Shore and Parry [2]. The crystal structure of the complex was studied by Lippert and Lipscomb [3]. The decomposition of BA was first investigated by Hu et al. [4] and its application as hydrogen source for fuel cell has already been proposed [5]. Thermal decomposition of BA takes place in the temperature range 77–137 °C. It was found that the complex completely decomposes at 1 1 2 °C releasing 1 mol of hydrogen per mole of complex [5]. This temperature is higher than the working temperature of polymer electrolyte membrane (PEM) fuel cell that is around 90 °C. At higher temperatures water evaporation strongly decreases PEM conductivity. For practical application of BA complex as hydrogen source for PEM fuel cell the decomposition temperature of the complex should be reduced.

Mechanical alloying (MA), a solid-state powder processing technique originally developed to produce oxide dispersion [6], has now been shown capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases. The synthesized non-equilibrium phases include supersaturated solid solutions [7,8], metastable crystalline and quasicrystalline phases [9], nanostructures [10], and amorphous alloys. MA of BA complex could be effective to improve the reaction kinetic. Doping the material with platinum could be also beneficial for hydrogen release.

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It was recognized that powder mixtures can be mechanically activated to induce chemical reactions, i.e., mechanochemical reaction (MR) at room temperature [11]. BA is a mild, efficient reducing agent for aldehydes and ketones [12] and it could reduce platinum ions to form platinum metal.

In this work we studied the effect of MA and MR with hydrogen hexachloroplatinate on the decomposition process of BA complex.

2. Experimental

BA complex (BH_3NH_3, Aldrich, tech. 90%) and hydrogen hexachloroplatinate(IV) hydrate ($H_2PtCl_6 + xH_2O$, Aldrich, 99.9%, Pt 38–40%) were used as-received. BA complex for MA or a mixture of the complex with the acid for MR were weighed to form 1.5 g batches which were loaded in a stainless steel vial together with two stainless steel balls. The vial was evacuated and filled with hydrogen. It was mounted in a shaker mill (SPEX 8000, CertPrep, Metuchen, NJ) and milled for 2 min followed by a 10 min pause. The sequence was repeated eight times. The total milling time was 16 min. Two doped samples with 1.0 and 2.0 mol% platinum were prepared. No macroscopic modifications were observed for the MA sample. The colour of the doped samples changed from white to dark grey.

The materials were characterized by X-ray diffractometry (XRD) analysis (Philips PW 3710 diffractometer) using Cu Kα radiation. The platinum grain size (D) was calculated using the Scherrer formula [13]: $\beta \cos(\theta) = k\lambda/D$, where β is the full-width-at-half-maximum length of the diffraction peak on a 2θ scale and k is a constant here close to unity. The value of D was computed from the (1 1 1), diffraction peak (the best resolved in the diffractograms).

Powders morphology was studied by scanning electron microscopy (SEM, Jeol JSM-5510LV). Energy dispersive X-ray spectroscopy (EDS) analysis was performed with an IXRF EDS-2000 System. The conditions were: accelerating voltage 25 kV, spot size 21 and working distance 21 mm. The powder specimens were directly deposited onto a conductive carbon double face tape, which was previously mounted on a SEM slab.

Thermal decomposition was monitored with the home-made measuring apparatus illustrated in Fig. 1.

Before each measurement the sample (about 50 mg batches) was introduced in a cylindrical glass holder equipped with a glass piston to eliminate the dead volume. By using a four-way valve the sample holder was alternatively connected with a vacuum pump, a 5% argon/hydrogen gas mixture, and the measuring apparatus. Before each measure the holder was evacuated and filled with the argon/hydrogen mixture for three times and finally connected with the measuring apparatus. The latter consists of a 50 ml graduate burette filled with a 1.0 M solution of $LiClO_4$ in propylene carbonate. To monitor the volume variations as a function of time and temperature, the resistance of the solution was recorded between two nickel electrodes fixed inside the burette. The resistance was evaluated measuring the voltage drop when a very small alternating current flows into the circuit. The volume of the displaced solution was directly read from the burette and used to calibrate the conductimetric cell response.

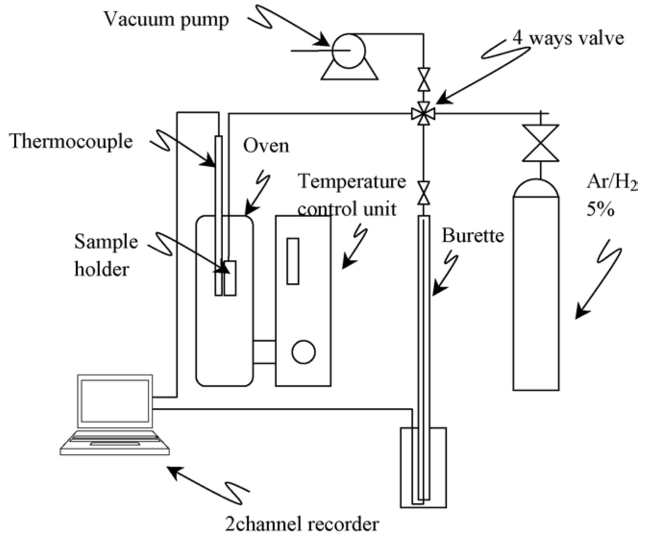

Fig. 1. The experimental apparatus for thermal decomposition measurements.

A thermocouple positioned close to the sample holder was used to record the temperature. The oven was heated at fixed temperature and, when the temperature was reached, the sample and the thermocouple were introduced into the oven. Both the signals from thermocouple and conductimetric cell were digitally recorded.

3. Results

3.1. Material characterization

BA complex obtained from the market is a technical product with 90% of purity. XRD spectra for the as-received sample and the MA sample are showed in Fig. 2. All the peaks can be indexed to BA (JCPDS card no. 13-0292) [14]. Fig. 3 shows an enlargement of the regions where the most representative peaks related to BA are located. The as-received sample shows narrow peaks and a family of peaks strictly correlated to the main one. The BM sample shows a decreasing of the satellite peaks. This behavior can be related to a increasing symmetry in the ball milled sample.

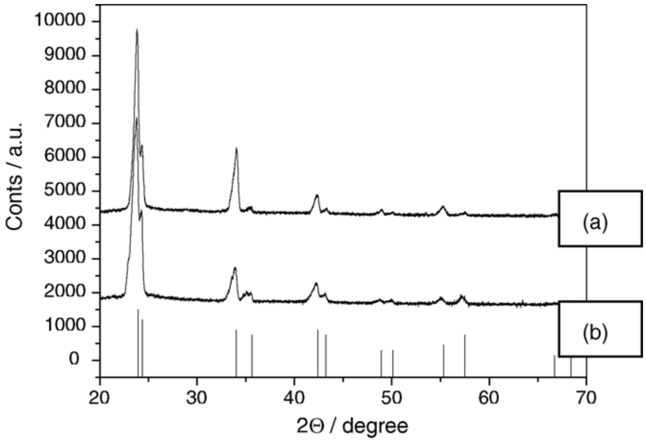

Fig. 2. XRD spectra of as-received (a) and MA (b) NH_3BH_3 sample.

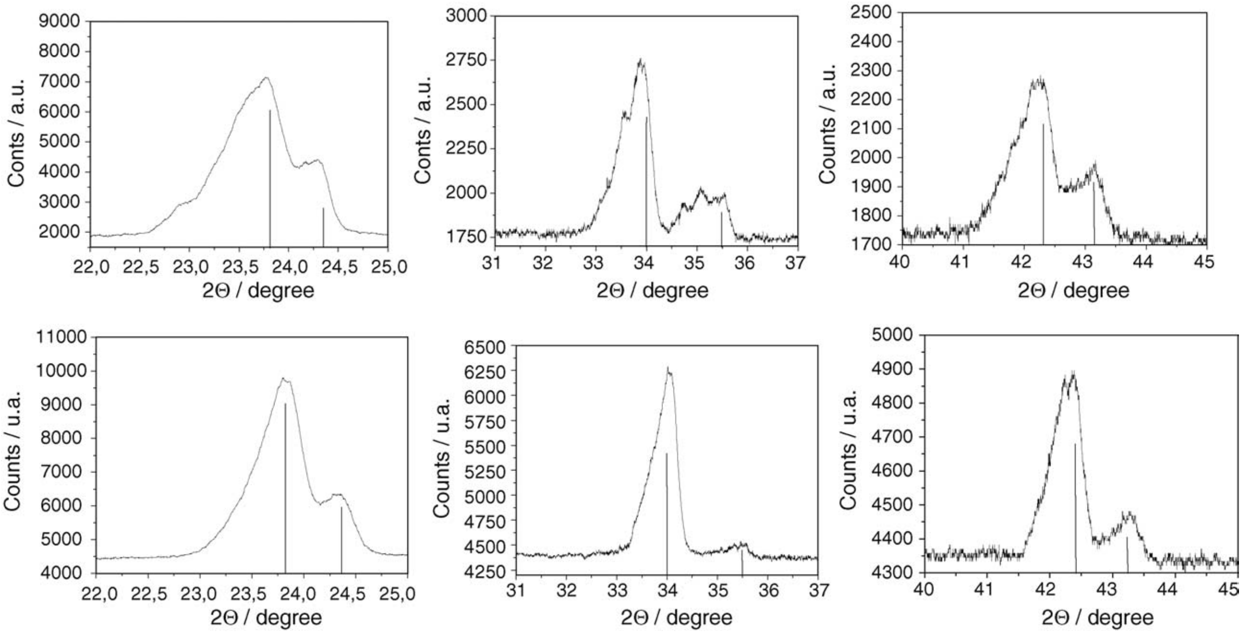

Fig. 3. Details of the BA peaks of Fig. 2; the upper three are for the MA sample, the lower ones are the corresponding angle peaks for the as-received sample.

XRD spectra for the 1 and 2 mol% platinum MR samples are showed in Fig. 4(a). There is a strong reduction of the peak intensities related to the BA complex and the appearance of new very broad peaks. The peaks at 39.7°, 46.2°, and 67.4° can be ascribed to platinum metal (JPDC no. 04-0802). Fig. 4(b) and (c) are a zoom of Fig. 4(a) and show the [1 1 1] platinum reflection peak. The platinum grain size (D) was about 9.39 nm and 9.16 nm for the 1 and 2 mol% doped samples, respectively. Two broad peaks located at 26.9° and 32.0° were unidentified, they could belong to intermediate reaction products. It is worth to note that other compounds containing platinum and chlorine have peaks located in these regions.

3.2. Morphological investigation

The morphological features of the four samples are showed in Fig. 5. The SEM image of the as-received BA (Fig. 5(a)) shows a disorganized structure. The presence of some fibres, arranged to leave some holes, could suggest reef-type morphology. When BA is subjected to ball milling the material loses its original size and the aggregate dimensions are reduced (Fig. 5(b)). It is worth to note that the fibre-like morphology is still retained and material surface looks like foam. The incorporation of 1 mol% H_2PtCl_6 during ball milling induced a transformation in the sample morphology and a more dense structure takes place (Fig. 5(c)). The material presents several holes, some of these having white contours are covered with a thin layer, so they look like bubbles. The increase in the amount of H_2PtCl_6 (2 mol%) increases the bubble number and dimension (Fig. 5(d)). The map analysis of the elements of the doped samples showed that Pt and Cl are homogeneously distributed on the samples as showed in Fig. 5(e) for the 1 mol% doped sample. The white spots on the material surface were identified as metal platinum by EDS.

3.3. Thermal decomposition

Fig. 6 shows the time evolution of the decomposition reaction of BA complex as-received (Fig. 6(a)), after MA (Fig. 6(b)) and MR with 1 mol% Pt (Fig. 6(c)). It was assumed that the gas evolved in the decomposition process was hydrogen and in the figures the hydrogen weight percent with respect to the weight of the sample is reported as a function of time. In further analysis the decomposition is assumed to be a first order reaction. At 95 °C, the decomposition rate for the as-received sample (Fig. 6(a)) is very slow and after 4500 s about 3% hydrogen was desorbed. By increasing the temperature the same amount of hydrogen is desorbed in shorter times and the final desorbed amount slightly increased. The maximum hydrogen amount desorbed at 140 °C after 4500 s was 5.2%. The melting point of NH_3BH_3 (110 °C) lies in the middle of the explored region. As a consequence, the data are collected from solid or partially melted materials. Anyway, the effect of phase transition does not seem to affect the decomposition times and rates.

The milled sample shows decomposition time of the same order of magnitude of the as-received sample but increased amount of desorbed hydrogen. The hydrogen released at 4500 s and 90 °C was about 4% and it increased to 6.4% at 140 °C. In the case of 1 mol% doped sample the decomposition process started at temperature lower than the as-received and MA sample. At about 73 °C the decomposition was already well established. By increasing the temperature up to 83 °C about 3% hydrogen was collected in 4500 s and a maximum of 7.5% was measured at 150 °C. The 2 mol% doped sample showed faster kinetics and it promptly reacted at temperature as low as 70 °C.

Fig. 7 shows the time dependence of the hydrogen evolution for the 1% doped sample heated at 73 °C. Less than 0.5% hydrogen develops at temperature lower than the equilibrium

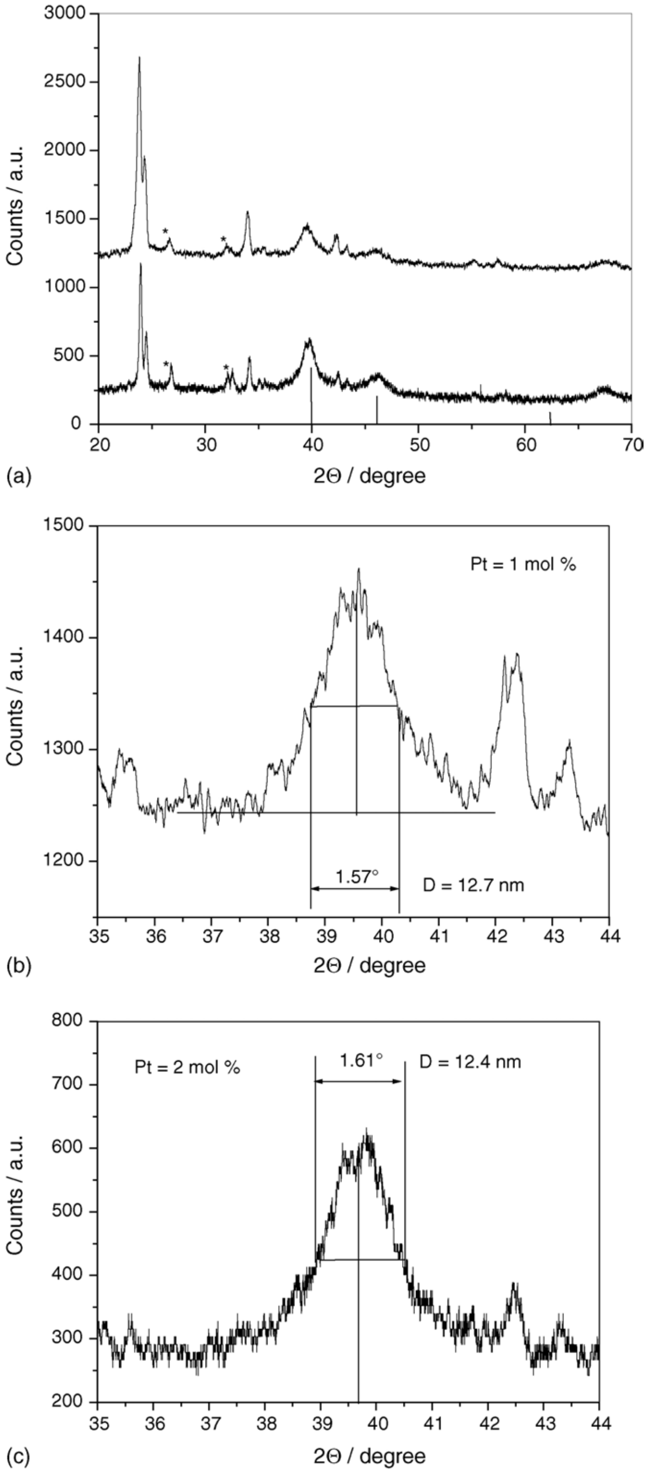

Fig. 4. (a) XRD spectra for the 1 and 2 mol% platinum MR samples; (b, c) zooms of the peaks in (a) related to [1 1 1]Pt.

one. About 1.5% hydrogen was collected during a fast kinetic process at 73 °C and a third slower decomposition process, observed at longer time, contributes for additional 1% hydrogen. The final amount of hydrogen desorbed in 6 h run was 3%. The characteristic time of the reaction (τ) was evaluated by calculating the time corresponding to the maximum of the volume/time derivative curves.

Fig. 8 shows the Arrhenius plot of the kinetic constants, as obtained from τ ($k = \ln(1/2)/\tau$); the as-received and the MA sample show similar behaviour and the points are scattered on the same curve. Referring to the pristine sample, the 1 mol% doped sample showed better desorption kinetics. The lower curve is related to the further decomposition process appearing only in the doped material.

Fig. 9 shows the amount of hydrogen released from the 1 mol% doped sample as a function of the sample temperature. In the figure the oven temperature is also reported. The latter was always lower than the sample one. By increasing the oven temperature until 120 °C it results an increase of the desorption temperature (that increase up to 105 °C). The desorption temperature did not change by further increasing oven temperature. A decomposition process was observed for temperature higher than 100 °C with the decomposition temperature increasing with the oven temperature.

4. Discussion

The hydrogen desorbed at 95 °C from BA complex as-received was 3% that is less than the 50% of the theoretical value (6.49%) as calculated from reaction (1):

$$BH_3NH_3 \rightarrow -(BH_2NH_2)- + H_2 \qquad (1)$$

The volumetric titrations reported in the work of Wolf [15] showed that 1 mol of hydrogen is desorbed at 90 °C in few hours. The amount of hydrogen released in our experiment is lower than the previously reported one. This result cannot be explained taking in consideration only the material purity (90%). We observed that part of the material is pushed up from the thermalized zone as a consequence of the thermal decomposition, remaining non-reacted.

The MA produced a material that showed increased hydrogen desorption properties. At 96 °C the amount of hydrogen released in 1 h was about 4% and the theoretical amount, corresponding to one hydrogen per mol of BA complex, was released at 136 °C. The changes in the morphology induced by MA could be both responsible for the enhanced gas evolution.

The doped sample spectra showed the presence of nano-scale platinum metal particles well distributed on the material surface. The following chemical reaction (2) can be evoked for platinum displacement:

$$2H_2PtCl_6 + 3BH_3NH_3 \rightarrow 3BCl_3 + 2Pt + 3NH_4Cl + 5H_2 \qquad (2)$$

Hydrogen and boron chloride are gaseous species (boiling point for BCl_3 is 12 °C) and gas evolution was expected as result of MR. From Eq. (2) the ammonium chloride should be present but this compound was not identified by XRD spectra. Anyway, Eq. (2) should be regarded as one the possible pathway leading to metallic platinum. Other intermediate reactions could be involved in the process and the unidentified peaks located at 26.9° and 32.0° could be related to intermediate platinum–chlorine adducts.

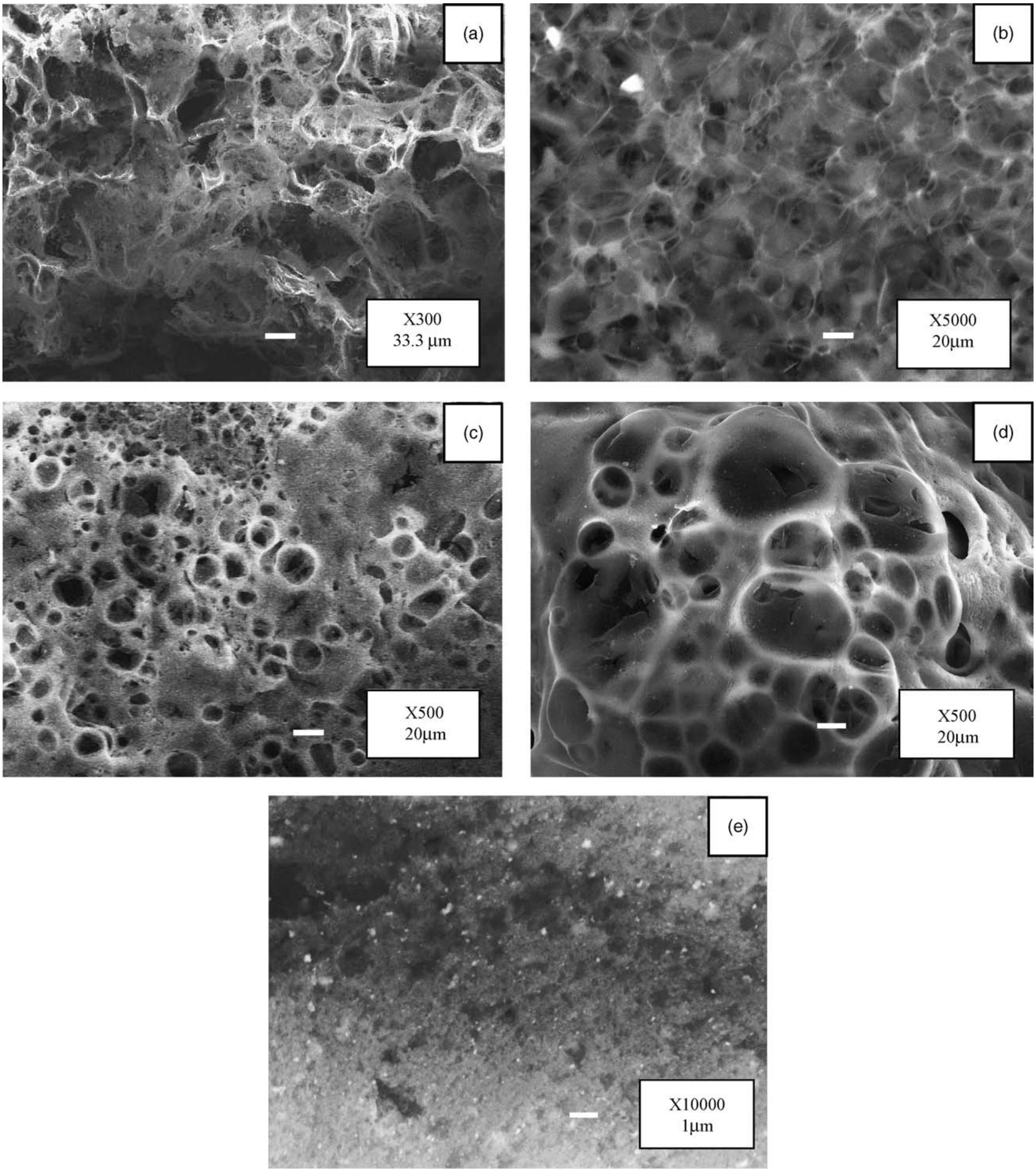

Fig. 5. SEM images of as-received BA (a), ball milled BA (b), with 1 mol% H_2PtCl_6 (c, e), with 2 mol% H_2PtCl_6 (d).

The presence of bubbles as observed by SEM indicates gas evolution and this could be related to gaseous product formation during MR (hydrogen and/or boron chloride). Evolution of gaseous hydrogen, produced during MR and trapped inside the material, could be correlated to the first decomposition step as observed by volumetric titration at 70 °C (see Fig. 7). The second step is the decomposition of BA as described in Eq. (1). Finally the third step could be related to hydrogen evolution coming from the decomposition product catalyzed by the noble metal Eq. (3) or other gaseous species as described by the work of Wolf et al. [15].

$$-(BH_2NH_2)-\xrightarrow{Pt}-(BHNH)-+H_2 \qquad (3)$$

Considering only the second step, the total amount of hydrogen released from the doped sample at 103 °C is about 3.5%. This value is lower than the one showed by the milled sample (4.2%). This result can be related to hydrogen consumption: (a)

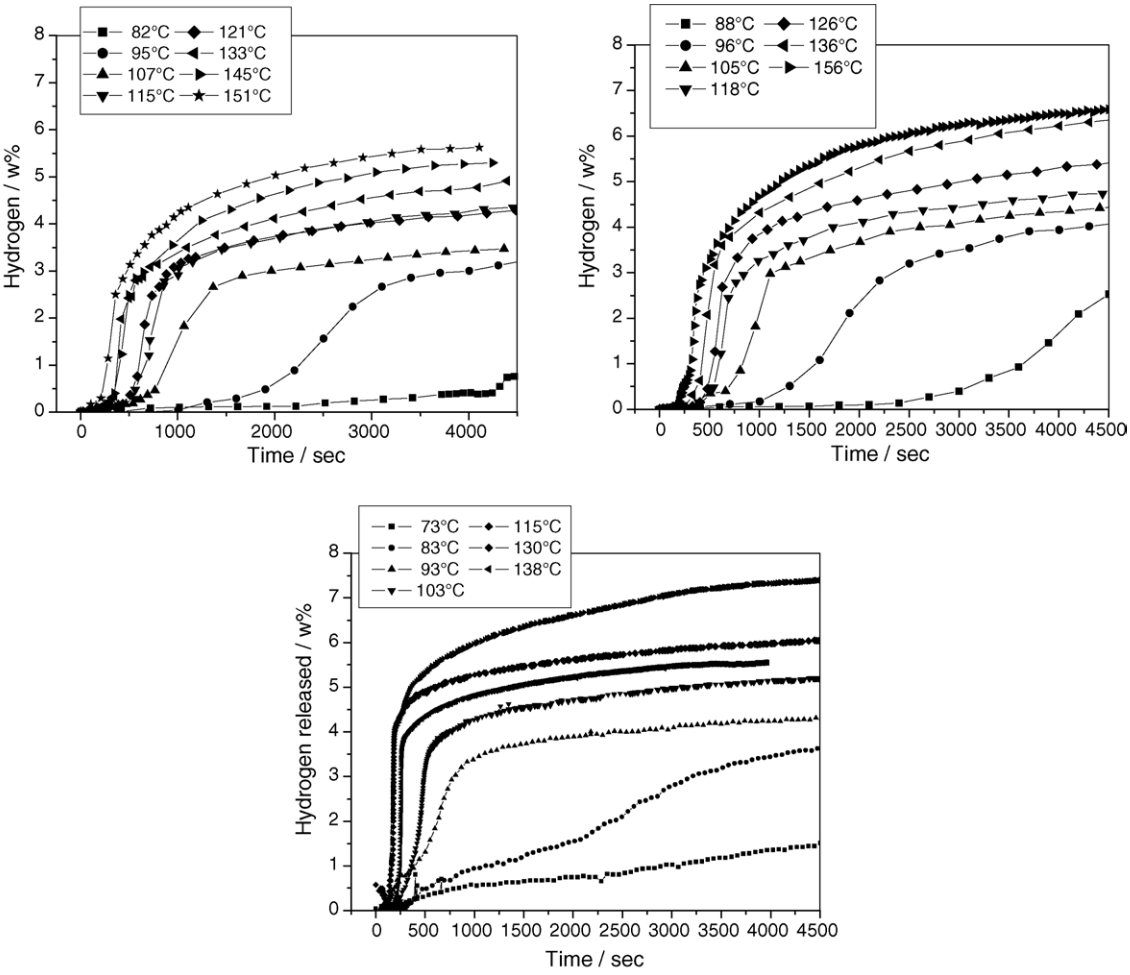

Fig. 6. Time evolution of the decomposition reaction of BA complex as-received (a), after MA (b) and MR with 1 mol% Pt (c).

for platinum reduction as illustrated in Eq. (2); (b) for water molecules reduction as described in Eq. (4). Water adsorbed on hydrogen hexachloroplatinate acid (about 1:1 mol) can react with the BA complex decreasing the hydrogen content.

$$2BH_3NH_3 + \tfrac{3}{2}H_2O \rightarrow B_2O_3 + 2NH_3 + \tfrac{9}{2}H_2 \qquad (4)$$

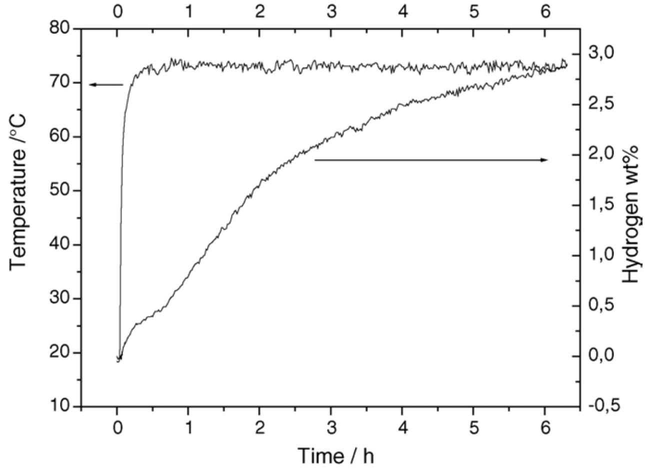

Fig. 7. Time evolution of hydrogen desorption for the 1% doped sample heated at 73 °C.

The 2 mol% doped sample showed higher decomposition rates. The use of larger amount of expensive platinum was not reputed convenient with respect both economic as well as technical point of view (decomposition temperatures lower than fuel cell working temperature were achieved).

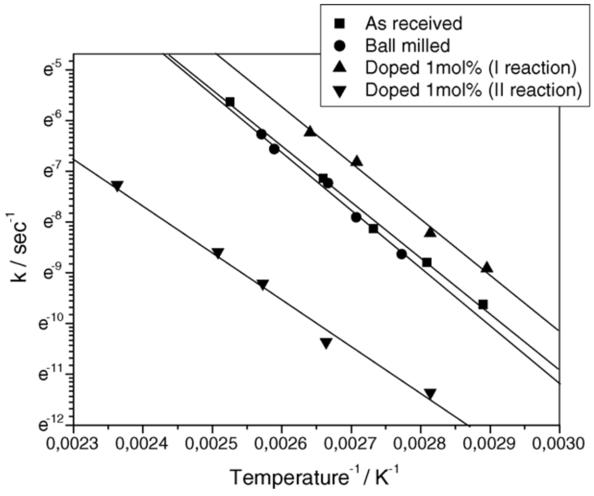

Fig. 8. Arrhenius plot of the kinetic constants.

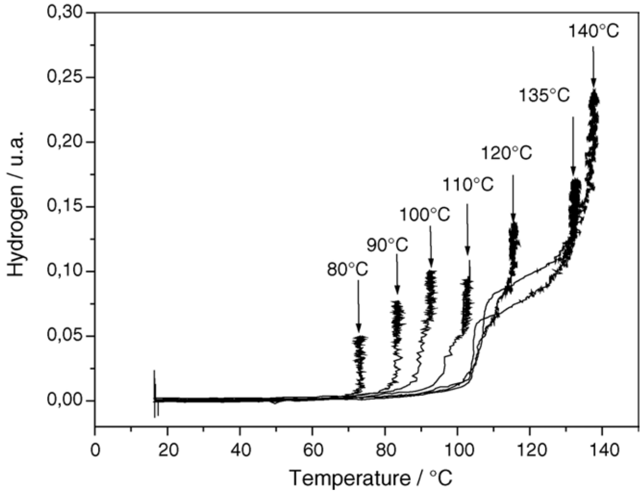

Fig. 9. The amount of hydrogen released from the 1 mol% doped sample as a function of the sample temperature. The nominal temperature is also reported.

5. Conclusions

It was found that nano-sized platinum metal is formed as result of MR of BA complex. The decomposition temperature of the 1% mol Pt doped sample match the working temperature of PEM fuel cell. As result the thermal decomposition of doped BA could be an efficient way to produce hydrogen on demand at convenient and safe low pressure. Evolved gas detection as well as solid decomposition product analysis should be conducted to evaluate hydrogen purity and clarify the effect of the catalyst on the decomposition reaction. Further research activities are on going to study the effect of less noble metals as catalyst on the decomposition reaction of BA complex.

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