

Catalyzed hydrogenation of solid alkynes: an example of supramolecular enhanced catalytic hydrogenation reaction

Ilan Pri-Bar^{*}, Jacob E. Koresh

Nuclear Research Center Negev, P.O. Box 9001 Beer-Sheva 84190, Israel

Received 17 June 1999; received in revised form 9 August 1999; accepted 13 October 1999

Abstract

An unusual catalyzed hydrogenation reaction of solid pheylalkynyl derivatives in the absence of a solvent is studied.

The unique solid state catalytic reaction of a pheylalkynyl substrate precoated on a supported metallic catalyst is being explained in terms of supramolecular chemistry. The formation of molecular aggregates of the alkyne substrate in a close proximity to the transition metal enables a fast catalytic process in the solid phase. Catalytic sites are created via molecular recognition and self-assembly mechanisms. The accessibility of the metallic catalyst to the molecular stacks of the substrate enables a fast catalytic reaction in the absence of a solvent. The kinetics of the hydrogenation reaction is interpreted and explained via self-assembled stacks that are constructed as a result of the well-known π - π interaction between pheylalkynyl molecules. XRD and TGA characteristics of the supported substrate also indicate the formation of substrate-catalyst sites, which have different characteristics from the pure substrate. The dependence of the hydrogenation kinetics on the type of catalyst support, size of the molecular stack, and catalyst concentration is studied. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalyzed hydrogenation; Gas–solid reactions; Alkynes; Phenyl acetylene derivatives; π - π interaction; Molecular stacking; Supramolecular chemistry

1. Introduction

The efficient catalyzed reaction between undissolved solid alkynes and hydrogen was applied for the preparation of “hydrogen getter” more than 20 years ago [1–3]. However, there was no appropriate interpretation of the nature of the interaction of a localized solid reactant with the dispersed supported catalyst.

Although the peculiarity of the solid state catalyzed reaction was recognized, the rationalization for this reactivity was that an increase in the mobility of the organic molecule enables this unique catalytic activity [1–3].

While in a conventional catalytic process, which takes place in a solution or gas phase, the substrate is in molecular form and its mobility enables catalyst–substrate collisions. There is no such molecular mobility in a solid system.

Therefore, a solid substrate would undergo a catalytic process only if the substrate molecules

^{*} Corresponding author.

are pre-arranged in closed proximity to the catalyst.

In the present article, the existence of a structurally defined aggregate of solid alkyne attached to the catalyst sites is suggested as an explanation for the unique fast hydrogenation reaction of undissolved solid alkynes. Kinetic measurements, XRD and DSC experiments support this explanation.

Existence of molecular “stacks” offers a simple explanation for the catalytic reactivity of a solid undissolved organic substrate toward hydrogen gas.

This type of reactivity could be described by the concepts of supramolecular catalysis rather than by molecular catalysis.

Supramolecular chemistry is a broader concept of material property [4,5], in which the “chemistry beyond the molecule boundaries” is being comprised. According to this concept, besides atoms and chemical bonds, there are other important chemical properties of the materials. These additional properties are determined by the nature of intramolecular interactions. Non-covalent forces and intramolecular interactions influence chemical reactivity. Molecular recognition, self-organization and molecular self-assembly are among the strategies in which nanostructures are being prepared [6,7].

Thus, a spontaneous assembly of several molecules into an aggregate could create an organized structure in which chemical reactivity depends to a great extent on the information stored in the polycomponent feature.

There are many examples of the formation of large, stable and structurally defined aggregates of molecules through hydrogen bonds, Van der Waals interactions or other non-covalent links. The Van der Waals aromatic π stacking is one of them [8–10].

Phenylacetylene (PA) derivatives are known to form highly ordered columnar-discotic nanostructures, both in liquid and solid states [11,12].

The π - π interaction and aggregation of phenylacetylene macromolecules (PAM) were demonstrated to exist even in solutions [13]

where NMR spectrum of PAM was found to be dependent on concentration.

It was suggested [13] that such interactions were observed in PAM and not in isolated PAs, since the interaction between a pair of isolated alkynylbenzene derivatives are too weak to be detected unless they are amplified by a proper molecular architecture.

In the present work, we studied the enhanced hydrogenation of solid PA derivatives. This amplification of reactivity is discussed in the light of the possibility that the observed PA's reactivity is originated in supramolecular interactions.

2. Experimental

2.1. Methods and materials

Commercially available diphenylacetylene (PA1) was used without further purification, other PA derivatives were prepared by a palladium catalyzed coupling of PA derivatives with the appropriate mono- or di-bromobenzene [14].

Coupling products were purified by recrystallization and analyzed by NMR. Commercially available supported Pd catalysts such as Pd/carbon, Pd/silica gel, Pd/calcium carbonate, were used without activation.

Reactive PA/catalyst solid formulations were prepared by a reduced pressure evaporation of the PA's solution in the presence of the powdered supported palladium catalyst. HPLC grade solvents were used for the preparation of the PA solutions. Determination of hydrogenation kinetics was performed on a computerized volumetric system with 0.1–100 Torr pressure transducer (MKS Baratron model 122). Hydrogenation was performed at ambient temperature in several consecutive stages.

The hydrogen pressure introduced at the beginning of each stage was usually 10% of the total hydrogen capacity of the sample. Hydrogen pressure decrease was recorded during the reaction and additional hydrogen was added when 98% of the gas was consumed.

3. Results and discussion

Complete hydrogenation of PA1 was performed on a solid mixture consisting of PA1 and 5% Pd on carbon in molar ratio of 16:1 (PA1/Pd). A 95.2% of the calculated theoretical quantity of hydrogen was consumed during 17.6 h. Toward the end of the experiment, hydrogen consumption rate becomes very slow and therefore the experiment was stopped. The reaction profile of hydrogen loading vs. time of the complete hydrogenation is shown in Fig. 1. Hydrogen was loaded in eight consecutive portions and each point in Fig. 1 represents the time needed to consume 98% of each portion.

The hydrogenation of an excess of PA1 in the presence of a limited quantity of Pd (16:1 ratio) demonstrates the catalytic nature of this solid–gas reaction.

The time coordinate is presented in log scale since rates sharply decrease after 70% of hydrogen loading: 10 min is required to load 70% of hydrogen, while 5.9 h are required to load additional 1.2% hydrogen following 94% loading.

The hydrogenated product mixture is washed with chloroform and the soluble product (bibenzyl) is analyzed by IR and determined by HPLC.

No Pd leaching could be detected during substrate washing. When the washed catalyst powder has been recoated with PA1, the prod-

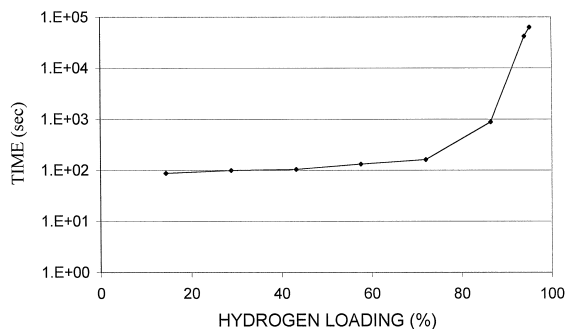


Fig. 1. Profile of a complete hydrogenation reaction of PA1 coated on Pd/C (PA1/Pd molar ratio of 16:1): percentage of hydrogen consumption vs. time.

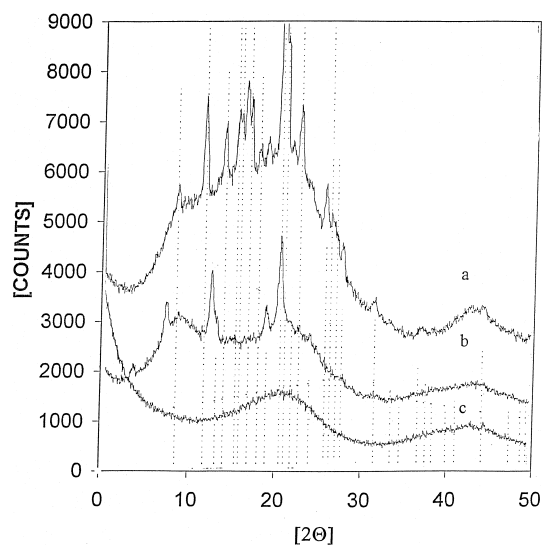


Fig. 2. XRD lines (a) of carbon and (b) of Pd/C 5% coated with PA1.

uct undergoes fast hydrogenation similar to Fig. 1. Thus, recycling of the catalyst is possible.

Since the amount of PA1 in the solid formulation is in excess of that amount needed to cover the catalyst with a single layer, one has to consider a multi-layer coating close enough to the Pd catalyst to permit interaction between the catalyst and PA1. As indicated in the introduction, the existence of structurally defined “stacks” of PA1 on the catalyst could assist the catalyzed reaction.

In the absence of Pd, the XRD analysis of charcoal coated with PA1 (Fig. 2a) exhibits a simple superposition of diffraction lines of crystalline PA1 and the pattern of the amorphous carbon (Fig. 2c). On the other hand, the XRD of 5% Pd/C coated with the same quantity of PA1 (Fig. 2b) shows distinctive diffraction lines which are different from these pure crystalline PA1. These lines could be interpreted as a result of the formation of organized PA1 stacks, similar to the packed structures found in other alkynylbenzene derivatives [8–12].

The kinetics of the hydrogenation reaction was studied by changing the molar ratio Pd/PA1. Assuming that PA1 is organized in stacks, this ratio also dictates the size of the

stacks: the higher the Pd/PA1 ratio, the smaller is the average size of the stacks. Fig. 3 (curves *a–d*) describes the calculated relative initial rates of hydrogenation, performed by introducing several consecutive portions of hydrogen as described in Section 2. The relative initial rates in each curve (*a–d*) are calculated at the points where 1% of the hydrogen portions have been consumed. At these points, H_2 pressure could be assumed to be constant throughout the curve. One can see that the initial rate increases along with the increase of the Pd/PA1 molar ratio (higher Pd concentration).

It should be noted that the amount of hydrogen introduced into the reactor is proportional to the quantity of PA1. Thus, the hydrogen pressure throughout curve (*d*) is lower than the pressure along the curve (*c*).

For higher Pd/PA1 ratios (Pd/PA1 = 1:8, curve *d*), the rates increase constantly during the progress of the reaction: the initial rate of the first stage is about one-half of the rate measured in the following fifth stage, after loading to 40% of the hydrogen capacity.

Lowering the Pd/PA1 ratio to 1:16 results in an increase in the reaction rates up to about 10% of hydrogen capacity and then decreases throughout the progress of the hydrogen loading process.

At lower Pd concentration, the reaction rates constantly decrease during the whole hydrogenation process.

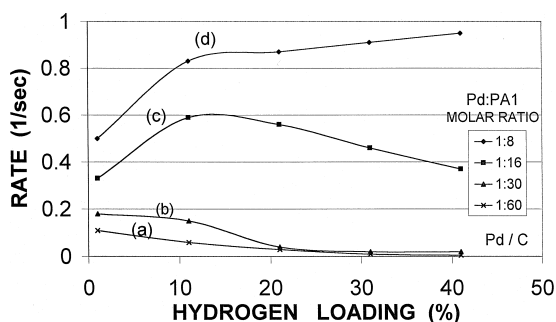


Fig. 3. Effect of PA1/Pd molar ratio on rate of hydrogenation of PA1 coated on Pd/C.

The initial rates of the first stages in each curve (*a–d*) are found to be proportional to the amount of Pd and inversely correlated to the hydrogen pressure and to quantity of PA1. Therefore, it is assumed that the initial rate is controlled solely by the catalyst activation step.

However, for samples with high Pd concentration, the slow catalyst activation step is not completed during the first stage and proceeds in the succeeding stages. Consequently, new active catalytic sites are formed successively, and the rate of hydrogen consumption continues to increase.

The step of hydrogenation of PA1 is thus associated with the catalyst activation step. Since the hydrogenation step seems to be relatively fast, it influences the total rate only after the completion of the catalyst activation.

With high Pd/PA1 ratio (Fig. 3, curve *d*), the continuous increase in the hydrogenation rate seems to be related to the fact that high Pd/PA1 molar ratio is associated with the formation of small stacks. In this case, the hydrogenation step is proceeding smoothly to completion.

On the other hand, at lower Pd/PA1 ratio (Fig. 3, curve *c*), larger stacks are formed. Stacks' distortions process, due to changes in molecular stereochemistry during hydrogenation, is believed to slow down the hydrogenation rate. Thus, subsequent to the activation of all the catalytic sites, a constant hydrogenation rate is expected, however, due to deformations in the stacks, reaction rates decrease at high hydrogen loading. In the same manner, very low catalyst concentrations (Fig. 3, curves *a–b*) result in large stacks and reaction rates are reduced already during the early stages of the process.

Hydrogen consumption rate for each portion of hydrogen in the hydrogenation of PA1 on 5% Pd/C is described in Fig. 4.

By plotting the kinetics of hydrogen consumption, the activation step could be noticed.

It can be seen that with Pd/PA (1:8) (Fig. 4a) the first portion is consumed at the lowest

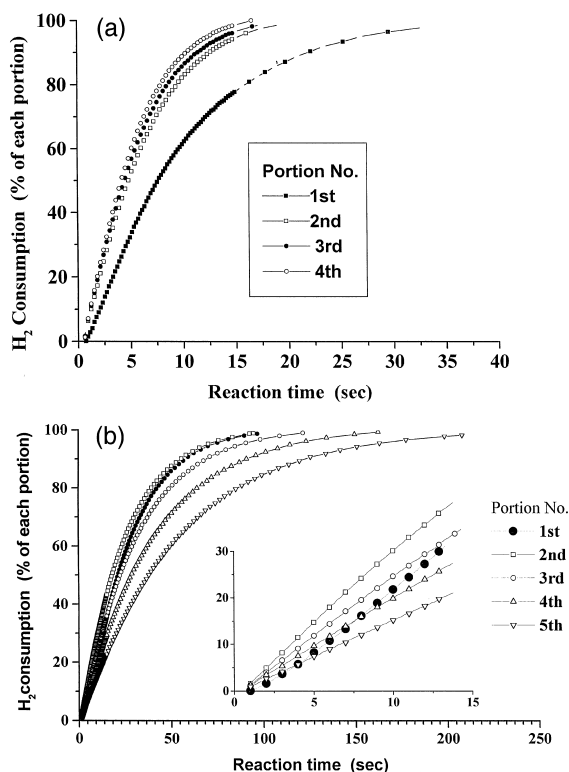


Fig. 4. (a) Consumption of five consecutive portions of hydrogen in the hydrogenation of PA1 coated on Pd/C (PA1/Pd ratio of 8:1). (b) Consumption of five consecutive portions of hydrogen in the hydrogenation of PA1 coated on Pd/C (PA1/Pd ratio of 16:1).

rate, while portions 2–5 react at continuously faster rates. (The curve of portion 5 is omitted from Fig. 4a since it superimposes the curve of portion 4).

On the other hand, at lower Pd/PA1 ratio, e.g., (1:16) (Fig. 4b), the second portion reacts slightly faster than the first one, while the reaction rates for the following portions decrease gradually.

By expending the 15 seconds region of Fig. 4b, an S-shaped initiation curve for the first hydrogen portion is noticed, a slow reaction rate at the beginning which accelerates toward the introduction of the second and third portions.

This kinetics can be explained by an initial rate determining step (e.g., activation of the catalyst) taking place only upon the introduction of the first portion of hydrogen.

A similar trend was found for 1,4-di(phenylethynyl)benzene (PA2) which is a considerably bulkier molecule than PA1 (Fig. 5). Since PA2 molecule contains two alkyne bonds, the alkyne bonds/Pd ratio is considered instead of the molar ratio.

The increase in the initial reaction rate (in each curve) is explained again by the slow activation step of the palladium catalyst, followed by a faster hydrogen transfer from the activated catalyst to the PA2s aggregates.

The rapid deterioration of the bulkier aggregates of PA2 is emphasized by the fact that even for the low alkyne/Pd ratio (e.g., 4:1), a decrease in the reaction rate is observed following the catalyst activation step, while in the case of PA1/Pd (8:1), a continuous increase in rate is observed (Fig. 3d).

In contrast to alkynes such as PA, a non-linear olefinic molecule with sp^2 configuration is regarded as less suitable for stacking. Indeed, non-planar [15,16] *trans*-stilbene was found to react very sluggishly (Fig. 6): very slow hydrogenation takes place and the total hydrogen consumption is limited to the stoichiometric hydrogenation of monolayer coating.

The non-catalyzed reaction of *trans*-stilbene strongly supports the assumption that the π - π interactions of the planar alkyne molecules contributes to the reactivity of the PAs and enables the catalytic reaction. Such π - π interactions assist in the formation of organized stacks in the

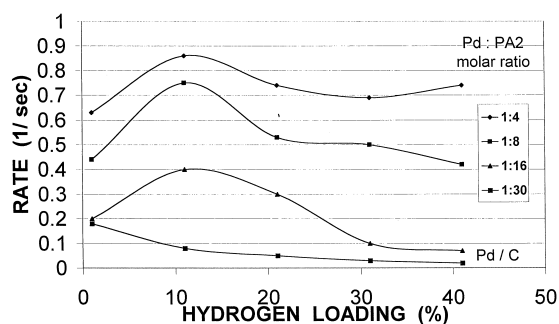


Fig. 5. Effect of PA2/Pd ratio on rate of hydrogenation of PA2 coated on Pd/C.

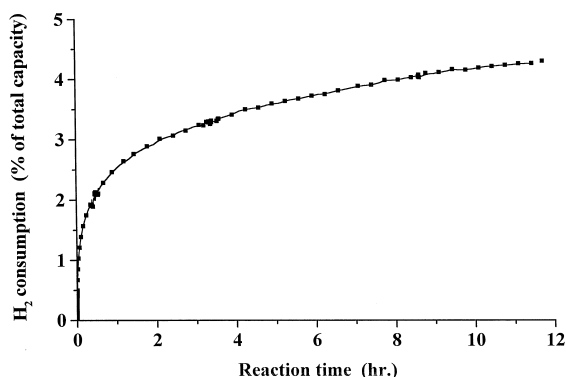


Fig. 6. Profile of the hydrogenation reaction of stilbene coated on Pd/C (stilbene/Pd molar ratio of 16:1): percentage of hydrogen consumption vs. time.

proximity of the Pd catalyst and thus facilitate the catalytic reaction.

The lack of planarity of *trans*-stilbene molecules in solution is most likely the cause that avoids its spontaneous aggregation. On the other hand, a “stilbene intermediate” is probably stabilized in the stack as more planar specie. The configurations of *trans*-stilbene in these two states resemble its configurations in gas and solid states: the twist angle of the phenyl from the vinyl group in *trans*-stilbene could exceed 30° in gas phase and 5° in solid state [15,16]. This could probably explain the unreactivity of *trans*-stilbene vs. the conceivable reactivity of a “stilbene intermediate” in the hydrogenation process.

The kinetics of hydrogenation depend also on the type of catalyst support. Two types of supports were employed: supports that are characterized by a relatively high initial rate, such as activated carbon (Fig. 3) and supports with a low initial rate such as Pd/CaCO₃ and Pd/BaSO₄ (Fig. 7).

The figure indicates that the initial reaction rates of the first portions are significantly slower than the rates measured in the advanced steps.

The differences in the reactivity of the supports is related to the fact that the surface area of carbon support is higher in an order of magnitude than that of CaCO₃ and BaSO₄ sup-

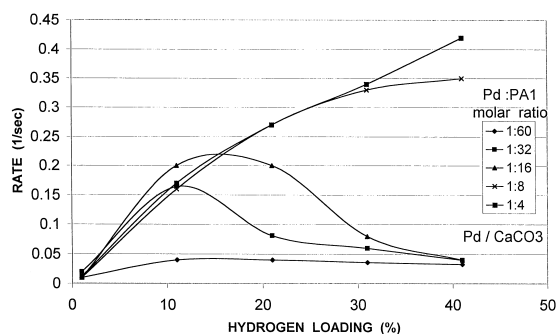


Fig. 7. Effect of PA1/Pd molar ratio on the rate of hydrogenation of PA1 coated on Pd/CaCO₃.

ports. One can speculate that in the case of carbon support, a fast adsorption of hydrogen from the gas phase accelerates the initial rate. An alternative explanation is related to the differences in the interactions of the supports with PA coating that affects the stabilization of the stacks around the catalytic sites.

A distinguished initiation process during the activation step of Pd/CaCO₃ is clearly shown in the curve describing the kinetics of hydrogen consumption, where a typical S-shaped curve is obtained during the reaction of the first portion of hydrogen (Fig. 8).

The activation process take place to a very small extent also with Pd/C (Fig. 4b, expanded

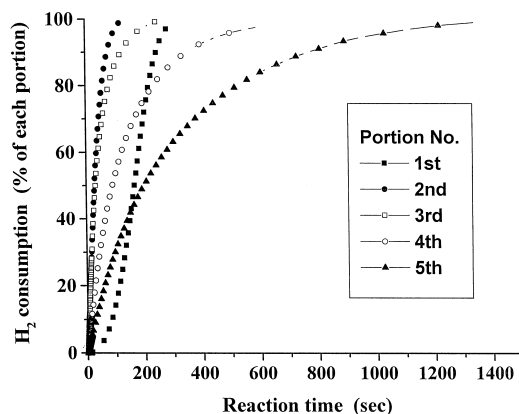


Fig. 8. Consumption of five consecutive portions of hydrogen in the hydrogenation of PA1 coated on Pd/CaCO₃ (PA1/Pd ratio of 16:1).

view), however, by using CaCO_3 support, the activation requires considerably longer periods.

PA's coating process determine the efficiency of the catalytic reaction and has a significant influence on the kinetics: various solvents used in the evaporation/coating process drastically affect the kinetics of the hydrogenation as demonstrated in the hydrogenation of PA1 coated on Pd/C (Fig. 9).

There is no single physical property of the solvent, which determines solely the efficiency of the stack formation. In general, using solvents with higher vapor pressure result in PA's coating with a higher reaction rate (ether > acetone > chloroform > THF).

However, the use of benzene and ethyl acetate results in a product which reacts rapidly in spite of the low vapor pressure of these solvents.

Thermal analysis measurements indicate that PA coated on a catalyst powder has different thermal characteristics at various loading ratios. PA1 stacks on Pd/ CaCO_3 produced in mole ratio 4:1 (PA1/Pd) gave a broad exotherm in the range 180–220° (Fig. 10b).

Heating to higher temperatures, up to 280°C results in a broad endotherm with a weight loss that corresponded to most of the PA1 mass (Fig. 10b). This is considerably different from the thermograph of pure PA1 that undergoes endothermic evaporation process at much lower temperatures 150–190° (Fig. 10a).

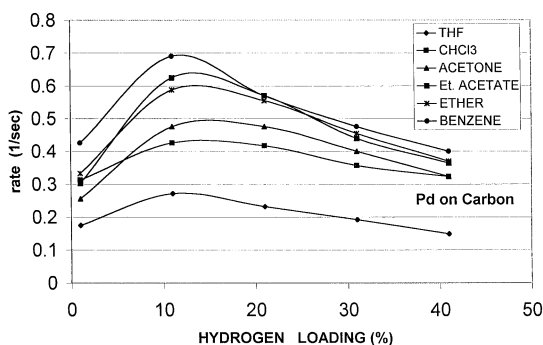


Fig. 9. The effect of various solvents used in the synthesis of PA1 stacks on the rate of hydrogenation of PA1 coated on Pd/C.

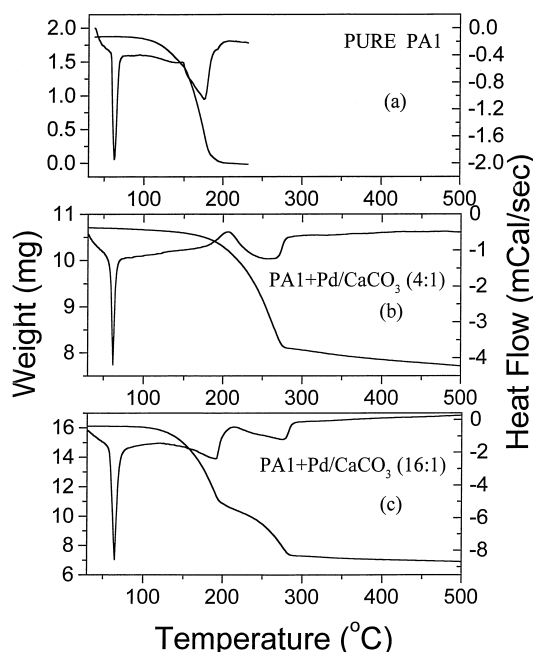


Fig. 10. Thermal analysis spectrum of PA1 coated on Pd/ CaCO_3 in various molar ratios.

PA1 stacks on Pd/ CaCO_3 produced in mole ratio of 16:1 have again significant different thermal characteristics: additional evaporation endotherm at lower temperature (150–210°) is demonstrated (Fig. 10c).

This supplementary endotherm is at the temperature range of the evaporation of pure PA1.

The endotherm at 220–280° (Fig. 10c) is therefore related to PA1 interacting with the metallic catalyst, while evaporation of PA1 which is remote from the metal takes place at lower temperature (150–210°). The two well-resolved endotherms can be recognized due to the existence of relatively large stacks. The 180–220°C exotherm (Fig. 10b) is related to chemical transformations of the stacked PA. At higher PA/Pd ratios the exotherm is covered by the 150–190° endothermic evaporation of PA1. MS analysis of evolved gas of supported PA1 at 500°C revealed fragments of masses 77 (C_6H_5) and 90 (C_7H_6) that are indicative of a decomposition process of the supported PA1.

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