Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 573–577

THERMAL STABILITY OF PLATINUM PARTICLES EMBEDDED IN MESOPOROUS SILICATES

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The thermal stability of platinum nanoparticles immobilized in SBA-15 silicate was investigated. The Pt nanoparticles were prepared in aqueous solution using polyvinyl-pirrolidone (PVP) as shape- and size controlling agent. The appropriate pretreatment conditions of cleaning the metal surface were determined.

Keywords: *IR spectroscopy, platinum in mesoporous silicate, thermal stability of platinum nanoparticles*

Introduction

Preparation of supported metal catalysts wrestles with several difficulties. Besides the heterogeneous particle size distribution, the homogeneous dispersion of the metal is not realized very often [1]. Most of the heterogeneous catalytic reactions take place on the terraces, edges and kinks of the metal particles and only some of them require metal atoms for the transformation. The number of active faces or places, i.e. the number of edges, clinks or terraces strongly depends on the morphology of the metal crystallites. If the size of the metal particle is not uniform, which is generally not guaranteed in the conventional preparation processes, even more inhomogeneity might be expected for such a catalyst. Furthermore, the selectivity of such catalyst in various reactions will be changed as well. From these it follows that there is a great demand to prepare catalysts with uniform particle size and morphology. How can we characterize these materials? The answer is that we require catalysts in which the metal particles are distributed homogeneously on the support and in which the metal particles possess identical size and crystal morphology. Why is it so important? – arises the next question? The reason of its importance can be found in the surface chemistry of single crystals. A great body of experimental results of the investigations of single crystals under very clean conditions, like in UHV, has been accumulated. Researchers proved that which metal face was active in a transformation and on which metal face opened new reaction paths leading to side reactions decreasing the selectivity [2]. Some years ago huge efforts started to increase the selectivity of a series of reactions since higher selectivity even with lower activity is considered as more environmental friendly solution.

From what we discussed above it follows that the aim of a research direction in our department is to close the characteristics of supported metal catalysts to that of the single crystals exhibiting excellent selectivity in several reactions. The first step we have done was the synthesis of metal particle with narrow particle size distribution and having well defined crystal morphology. For platinum we prepare particles with tetrahedral or cubic morphology. The experimental parameters influencing the particle size distribution are under investigations. The experimental conditions assuring the given morphology of the platinum particles have been elaborated.

Several support materials were tested. In this paper we report the results obtained with SBA-15 mesoporous silicate as support of the platinum particles.

The aim of this work was to investigate the thermal behavior of platinum particles supported on SBA-15 silicate. It is well known that for the preparation of metal particles with some nm dimensions and a given morphology surface protecting agent should be used. The role of this matter, generally some sort of polymer, is to settle down onto the growing crystal and stop the growth of the metal particle. However, this organic matter should be removed before use of the catalyst. The simplest way can be suggested to do that is to burn the organic components. But what will happen with the shape of the metal particles upon this burning. How can we get rid of the organic matter while we preserve the shape of the metal particles? These are the questions we discuss in this paper.

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1388–6150/$20.00

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Experimental

In the literature there are various preparation techniques to synthesize noble metal nanoparticles [3–5]. Platinum nanoparticles were synthesized according to Rampino and Nord [6] in aqueous solution of $1\cdot10^{-4}$ molar K_2PtCl_4 using polyvinyl-pirrolidone of M=40000 molecular mass (PVP), as surface protecting agent [7]. The PVP is extensively used in medicines and drugs as excipient and its thermal stability was studied by several researchers [8–10].

The synthesis procedure was as follows. The required amount of PVP was dissolved in distilled water. The estimated amount (to obtain 10^{-4} molar solvent) of platinum salt was added while stirring, for reduction hydrogen was used. First pure nitrogen was bubbled through the solvent for 20 min followed by reduction with hydrogen for 10 min. After stopping the gas streams the vessel was closed and stored in darkness for 12 h. The shape of particles was influenced by several parameters, such as the metal/protecting agent ratio, the temperature of crystallization, etc. The yellow colored colloidal solution of platinum nanoparticles was stored in refrigerator.

For the synthesis of SBA-15 type ordered mesoporous silicate tetraethyl-orthosilicate was used as silicon source while Pluronic P-123 triblock copolymer was the structure directing agent [11]. The TEOS:Pluronic P-123 ratio was 3:2 in the synthesis mixture.

The nanocomposite was prepared by impregnation of SBA-15 silicate with the aqueous solution of platinum nanoparticles. The suspension was sonicated for 2 h at room temperature. After the sonication the water was evaporated and the samples were dried and subjected to template removal process. For the latter the samples were heated to 770 K in air while the organic component was burned off from the sample. The platinum content was calculated to be 0.1 mass% on the support.

Two samples were prepared, containing cubic or tetrahedral platinum nanoparticles, and characterized by several physical methods. The TEM images were taken on a Philips CM10 type electron microscope. The particle size distribution of platinum particles was determined on the basis of the TEM images.

The surface area and the pore size distribution of the pure SBA-15 and its platinum loaded derivative were determined by a Quantachrome instruments NOVA 2000 series machine. Surface area was calculated using the BET adsorption-desorption method [12] and pore size distribution was analyzed by the BJH method [13].

Derivatographic experiments were performed in order to monitor the thermal behavior of the samples and to determine the temperature at which the organic matter of the surface protecting agent can be removed. For this 100 mg of samples were massed into a ceramic crucible and the TG-DTG profiles were registered using a Derivatograph-Q (Paulik–Paulik, MOM, Hungary) machine. The profiles were taken in the 298–1270 K temperature range.

For the IR spectroscopic investigations self-supported wafers were pressed from the samples and put into a sample holder which was placed in an in situ evacuable IR cell. After degassing at room temperature the base spectrum of the solid sample was registered. Then the temperature of the sample was increased by 50 K ramps to 770 K under vacuum. After each step a spectrum was taken.

The adsorption and reaction of cyclohexene was studied by IR spectroscopy as well. The clean organic matter free wafer was loaded to 10 Torr of cyclohexene or 10 Torr cyclohexene and 100 Torr of hydrogen and spectra were taken with increasing temperatures.

Results and discussion

Figure 1 shows the TEM images for cubic and tetrahedral platinum particles (the Pt:surface agent ratio was 1:1 and 1:5, respectively). The morphology difference can be clearly seen. The particles in Fig. 1a are dominantly cubic, while the particle size distribution is quite uniform. We found that the average particle size of these platinum nanocrystals is 3.57±0.67 nm. Figure 1b shows the tetrahedral platinum nanocrystals. Here again the particle size proved to be quite uniform and the average value was found to be 3.29±0.64 nm.

Figure 2a shows the TEM picture of the SBA-15 silicate. This material possesses hexagonally arranged tubular structure. It is a hard task to make good quality TEM picture from the platinum encapsulated in SBA-15 since it is a 3D system. But it is clearly seen, that the particles are not aggregated after the thermal treatment (Fig. 2b). The diameter of the tubes determined from the XRD profile (not seen) was 7.68 nm. The BET surface area of the sample was 646 $m^2\,g^{-1}$. This rather high surface area may assist to disperse the platinum nanocrystals homogeneously.

As we have indicated in the experimental, both the platinum particles and the support SBA-15 silicate contain organic matter. For the synthesis of mesoporous structures including the SBA-15 type organic compounds are used as structure directing agents. Among these compounds amines with long carbon chain, quaternary alkyl ammonium ions at least with one long carbon chain, triblock copolymers of the type of PEO-PPO-PEO can be found. The molecules of these surfactant type materials form micelles in aqueous solutions. These micelles may have rod shape and can form hexagonal arrangement. These micelles will be covered with silicate ions and form

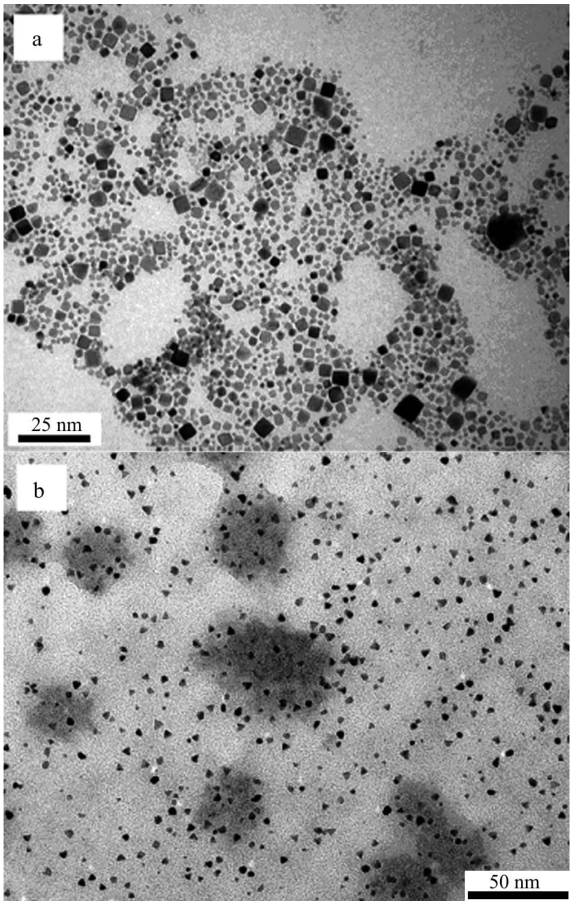

Fig. 1 TEM images of a – cubic and b – tetrahedral platinum particles (the Pt:surface agent ratio was 1:1 and 1:5, respectively)

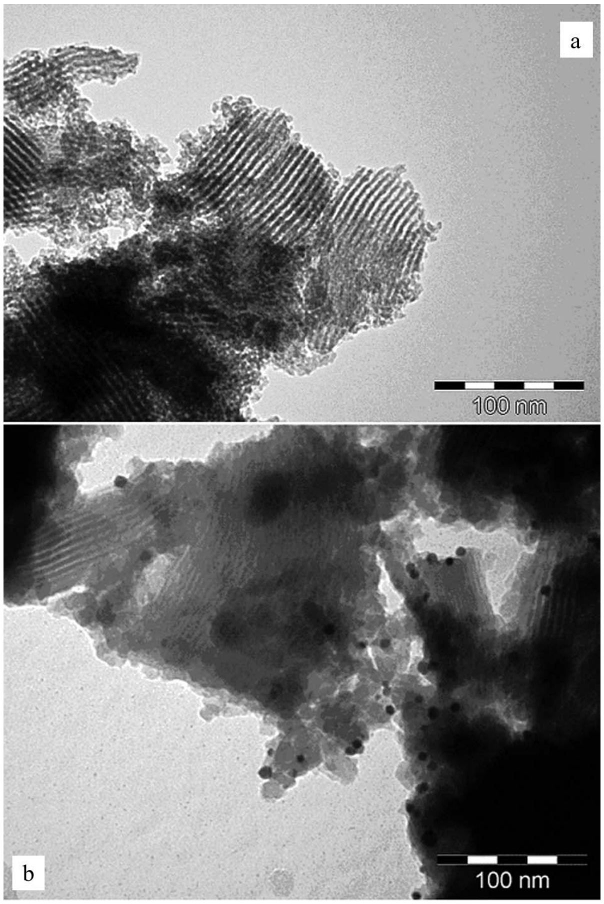

Fig. 2 TEM image of a – hexagonal mesoporous SBA-15 silicate and b – Pt/SBA-15 composite after heat treatment

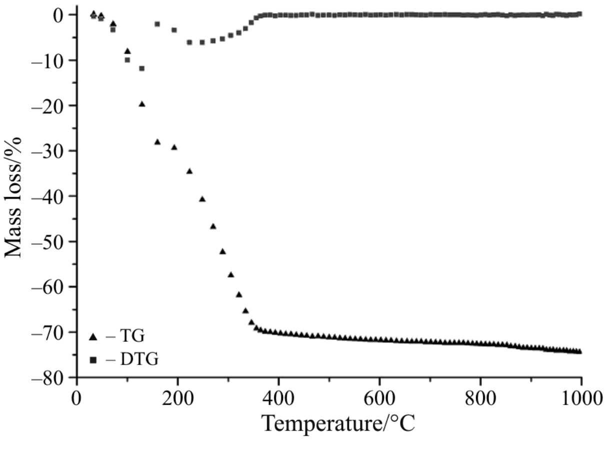

Fig. 3 TG and DTG profiles of as synthesized SBA-15 sample

arranged structures. After filtering, drying and washing the pure silicate structure has the arranged organic compounds in their original forms, i.e. rod like micelles are present. As these micelles fill the pores to have an adsorbent or a catalyst one should remove these organic molecules from the structure. Several procedures are known for removal of templates. The most frequently applied is the burning off. We choose this procedure for template removal. For determination of the lowest but appropriate temperature TG-DTG measurements were performed. Figure 3 shows the TG and DTG profiles of the as synthesized SBA-15 specimen. The most characteristic feature of this plot is that there is no mass loss above 770 K. Below there are two mass losses, the first is endothermic, the second appearing at higher temperature is exothermic. The first mass loss is due to the removal of adsorbed and loosely bond water from the structure. This process takes place with maximal rate at 380 K. The height of the step is 29%, that value is reasonable to the water adsorption capacity of such mesoporous silicates. The second mass loss is attributed to the burn off the organic template. This step occurs at 548 K and the height of the step is 40% revealing that the amount of template molecules is quite high. This is not surprising since these molecules should fill the pores assuring the very high surface area.

The surface of the platinum particles is covered by PVP polymer molecules and thus protect the nanosize metal *vs*. the further growing in the aquatic colloidal dispersion. Assuming that the PVP molecules have built an adsorbed layer on the Pt nanoparticles, after preparation of the supported material, the surface protected platinum particles are still present on the silicate surface. In this form the sample cannot be used as catalyst utilizing the activity of platinum metal, since the metal particles are encapsulated in the polymer shell. Thus, the metal surface is hindered to the adsorbate and/or reactant molecules. The surface protecting agent can be removed using an appropriate pretreatment. In reaction taking place in organic solvents this problem probably not comes up, since the organic reaction solvent dissolves the protecting compounds as well. This should be the case for the hydrogenation reaction of styrene over palladium nanocrystals supported on montmorillonite, although the authors did not give any details to this point [14]. We investigated the thermal behavior of platinum nanocrystals covered with PVP. It was not possible to investigate directly, as taking the TG-DTG patterns on the platinum nanocrystals since their concentration was low and we had not the chance to collect an amount required for derivatographic measurement. In order to get some insight into the thermal behavior of platinum nanocrystals, we investigated the TG-DTG profiles of supported metal. The supported catalyst, as we have described above was prepared using SBA-15 containing no organic matter. From this follows that when we investigate the supported sample the changes occurring at high temperature should be characteristic for the platinum component. Figure 4 shows the TG and DTG profiles of platinum supported on SBA-15. The first mass loss step is due to the removal of various adsorbed water forms. The second, hardly seen (please take into account that the concentration of platinum particles was less than 10^{-4} mol) slightly above 670 K is attributed to the removal of surface protecting agent. It is obvious also for us that this assignment should be supported by other independent experiments.

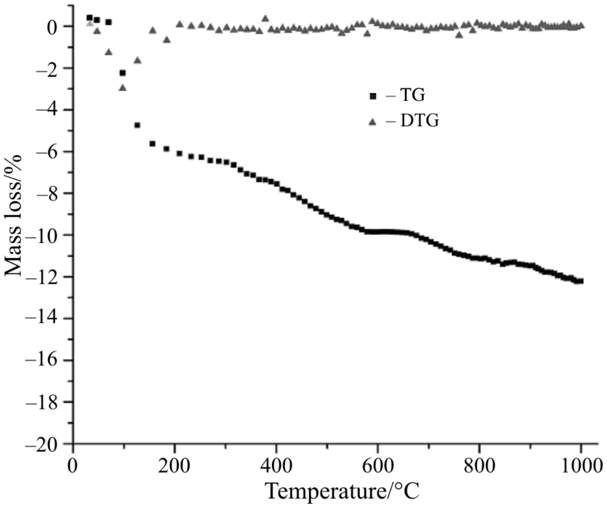

Fig. 4 TG and DTG profiles of platinum nanoparticles supported on SBA-15

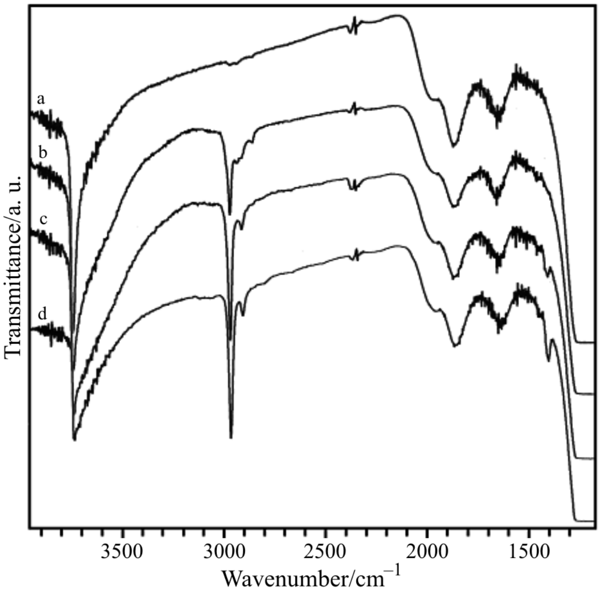

Fig. 5 FTIR spectra of differently pretreated Pt/SBA-15 samples

IR spectroscopy is an appropriate tool to monitor the surface of various solids. The self-supported wafer technique allows the researcher to test the clearness of the surface. This means that the characteristic absorptions of impurities existing on the surface can be detected with rather high accuracy. We performed IR spectroscopic experiments in order to shed some more light on the removal of platinum surface protecting compound. As can be seen in the IR spectra of nanocomposite treated under various conditions exhibited in Fig. 5, there is only one condition among the attempted ones which assures the complete removal of organic matter. When we treated the platinum supported sample in vacuum, at 723 K for 1 h a quite high intensity bands remained in the spectrum at around 3000 cm^{-1}. This group of band is characteristic of various CH vibrations. After treatment the wafer in 100 Torr hydrogen the result was similar, although the shape of the IR bands became simpler as can be seen in spectrum b. The treatment of the wafer in 100 Torr of oxygen, the bands due to the presence of hydrocarbon type materials are present. Any of these treatment procedures were not capable to remove the surface protecting compound sufficiently. The only procedure was the treatment of the sample in flow oxygen at 770 K for several h, which resulted in wafer with clean surface. The reason of the efficient cleaning is not understand perfectly yet. Further investigations are in progress. This IR result confirmed the finding of TG-DTG measurements.

We have performed preliminary experiments in hydrogenation and dehydrogenation of cyclohexene over the prepared supported platinum catalyst. When we used the samples containing surface protecting agent on the platinum particles no reaction was observed either for hydrogenation or for dehydrogenation. When the catalyst was clean, thus the capping agent was removed, both the hydrogenation and the dehydrogenation occurred. These results reveal the importance of the removal of surface protecting compound and by this to have the platinum surface able to catalyze reactions.

Conclusions

We have investigated the thermal behavior of supported platinum catalyst which has some novel characteristics such as (*i*) mesoporous silicate with a high surface area is the support of platinum nanoparticles, (*ii*) platinum nanoparticles have a well defined crystal shape, i.e. cubic and/or tetrahedral nanocrystals, (*iii*) these nanocrystals may mimic in the nanometer size regime the corresponding single crystal phases (100 and 111).

As such nanoparticles can be synthesized in aqueous solution of platinum ions in the presence of surface protecting compounds, in our case PVP. The appropriate pretreatment conditions were determined under which the metal surface was cleaned, thus the protecting agent was removed and catalytic transformation could occur on the metal surface. The removal of surface protecting agent was performed by burning the organic matter off at 770 K in oxygen flow.

Acknowledgements

The authors thank the financial support of the Hungarian Ministry of Education (OTKA T-037952, F-038249). ZK acknowledges the support of the Bólyai János Research fellowship.

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