Preparation and Catalytic Use of Platinum in Magnetic Core/Shell Nanocomposites

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ABSTRACT: Platinum (Pt) nanoparticles show high activity as catalysts in various chemical reactions. The control of the morphology of Pt nanostructures can provide an opportunity to improve their catalytic properties. The preparation of Pt-loaded iron-oxide poly-vinylbenzyl chloride nanocomposites was done in several stages: first by the formation of the core consisting of magnetite nanoparticles and second by the polymerization of vinylbenzyl chloride in the presence of the magnetic core particles. The third step is the amination of the chlorine group with ammonia, which leads to an ion exchange resin. Then, the Pt precursor (H_2PtCl_6) is attached by ion exchange. Finally, the Pt ions are reduced to Pt metal with $NaBH_4$. The obtained material can be dispersed easily and be used as a catalyst which can be separated after the reaction by magnetic fields. Characterization of the resulting metallic nanocomposites is evaluated by atomic absorption spectroscopy, thermal gravimetric analysis, transmission electron microscopy, infrared spectroscopy, and gas chromatography. The activity of Pt at magnetic core/shell nanocomposites was measured for the reduction reaction of cinnamaldehyde to cinnamyl alcohol. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1806–1811, 2013

INTRODUCTION

The outstanding potential of core/shell nanocomposites[1,2] stems from the ability to obtain structures with the combinations of properties that neither individual material possesses. It is possible to synthesize these nanocomposites in desired size and shape and with controlled improved properties such as increased stability, surface area, magnetic, optical, and catalytic properties.[3] The easy separation and controlled placement of these functionalized magnetic nanoparticles by means of an external magnetic field enables their application in catalyst supports. Transition metal containing core shell nanoparticles are particularly interesting because these systems can have multiple functions that do not exist in single-component compounds and unique properties that exist only in nanometer-sized materials.[4]

For instance, core–shell nanoparticles have been tested as catalysts in various chemical reactions, and both core and shell are actively involved in the catalytic processes.[5–11] The catalytic reactivity depends on size and shape of nanoparticles and therefore synthesis of controlled shapes and size of colloidal platinum particles could be critical for these applications. Platinum (Pt)–iron (Fe) nanocomposites show high activity as catalyst in

organic synthesis.[12] The smaller the metal particles are at the same metal loading, the larger are the fraction areas of metal atoms that are accessible to reactant molecules and available for catalysis. One of the most known methods used for preparing nanostructured metal particles is the transition metal salt reduction method.[13]

In most methods of preparation, two or four valence Pt is reduced to zero-valence metal atoms with a reducing agent, for example sodium borohydride ($NaBH_4$). The most popular procedure is the reduction of H_2PtCl_6. Most polymeric supports are insoluble, nonvolatile, nontoxic, and often recyclable, properties that are especially attractive in an area of enhanced environmental awareness.[14] Crosslinked polymers, which are insoluble in solvents, have been used in most polymeric supports. Depending on the degree of crosslinking, these networks can be swollen by selected solvents.

Polymer-supported catalysts use a polymer support in which catalytically active species are immobilized through chemical bonds or weaker interactions such as hydrogen bonds or donor–acceptor interactions. Polymer-supported catalysts[15] are often based on the network polymers in the form of beads.

They are easy to separate from reaction media and can be used repeatedly. The use of functionalized polymers, which serve as supports for reagents or catalyst, in combination with reactants has the advantages of an easy purification of the desired product and the ability to drive reactions to completion.[16]

One important hydrogenation reaction used in the fine chemistry industry is cinnamaldehyde hydrogenation as reaction in this study. The desired product of cinnamaldehyde hydrogenation is cinnamyl alcohol, an important additive in food industry, perfumery, and an intermediated in the production of certain pharmaceutics.[17]

The selective hydrogenation of cinnamaldehyde is investigated using Pt–Fe/C catalyst. The 1% (w, mass fraction) Pt-1.5% (w)Fe/C catalyst exhibited the highest activity and selectivity at 60°C, (2.5 h, and 4.0 MPa H2.[18] The catalytic activity of Pt -loaded montmorillonite catalysts and their selectivity towards cinnamyl alcohol were reported. The activity and selectivity of 1 wt. % Pt -loaded montmorillonite catalyst were found to be appreciable.[19] The selective hydrogenation of cinnamaldehyde is investigated using platinum catalysts supported on carbon aerogels with different textural and chemical properties. The presence of mesopores and the increase of the acidic character in the carbon aerogels lead to a higher catalytic activity and selectivity towards cinnamyl alcohol when compared with that obtained for the untreated materials.[20]

In this study, catalytic activity is added to magnetic polyvinylbenzyl chloride nanoparticles. Pt is used to form Pt–Fe nanocomposites for using it as a catalyst for organic synthesis. In our previous study,[21,22] we have already prepared magnetic polyvinylbenzyl chloride nanocomposites by miniemulsion polymerization with a diameter range from 10 to 20 nm. In this study, we describe the attachment of noble metals as heterogeneous catalysts by adding catalytic properties to this nanocomposite material of magnetic polyvinylbenzyl chloride nanocomposites and the measurement of its catalytic activity. The functionalization was done by amination of magnetic polyvinylbenzyl chloride nanocomposites (polymer support) with ammonia dissolved in organic solvent and subsequent ion exchange. H_2PtCl_6 was used as catalyst precursor. Finally, Pt ions were reduced to Pt metal by the reducing agent NaBH4. The obtained materials were characterized by transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS), and thermal gravimetric analysis (TGA). The activity of the prepared catalyst was measured for the reduction reaction of cinnamaldehyde to cinnamyl alcohol. Analysis was carried out using gas chromatography (GC).

EXPERIMENTAL

Materials
Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ammonium hydroxide (26% $NH_3 \cdot H_2O$), hexane, dichloromethane, vinylbenzyl chloride (VBC, 95%), hexadecane, sodium dodecyl sulfate (SDS), potassium peroxodisulfate, oleic acid (90%), H_2PtCl_6, and NaBH4 were supplied by Fluka AG (Seelze, Germany) and used as received.

Preparation of Polymer Support of Magnetic Polyvinylbenzyl Chloride Nanoparticles by Using Miniemulsion Polymerization
Synthesis of the polymer support of magnetic polyvinylbenzyl chloride nanoparticles takes place in two steps. The first step is the formation of magnetite iron oxide nanoparticles by coprecipitation of an aqueous solution of $Fe^{3+}/Fe^{2+} = 2 : 1$ with concentrated ammonium hydroxide in excess. The second step is polymerization of VBC and magnetic nanoparticles in the presence of SDS as surfactant by using miniemulsion polymerization as illustrated in our previous study.[21,22]

Synthesis of Polymer-Supported Pt Catalyst on Magnetite Polyvinylbenzyl Chloride Nanoparticles
Polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles is formed in three steps as describe in the following sections[23]:

Amination of Magnetite Polyvinylbenzyl Chloride Nanoparticles

In brief, 12 mL of magnetite polyvinylbenzyl chloride dispersed in acetone is added to the mixture of 80 mL of ammonia in 50 mL toluene. The resulting solution is heated at 70°C for 6 h with stirring under reflux, producing deep black precipitates and then it is washed by acetone. After separating the magnetic product by a magnetic bar, it is treated with HCl (4%). The free acid is removed by water to form magnetite polyvinylbenzyl quaternary salt.

Ion Exchange. In all, 8 mL of H_2PtCl_6 solution (5 mM) in isopropyl alcohol is added to 0.5 g of magnetite polyvinylbenzyl quaternary salt. The adjustment of a basic pH value is done by some drops of NaOH and stirring at room temperature for 24 h.

Reduction by NaBH4. NaBH4 (0.016 g in 10 mL of isopropyl alcohol) is added to the mixture and stirred at room temperature for 24 h. The product is then washed with isopropyl alcohol to remove the excess of H_2PtCl_6 and NaBH4. Treatment with 10 mL HCl (4%) and removing the free acid by washing with water and separation of the prepared material by a magnetic bar leads to the final catalyst.

Catalytic Testing on Reduction of Cinnamaldehyde
Cinnamaldehyde (0.15 g), sodium borohydride (0.04 g), catalyst (0.00066 g), and methanol (9.9 g) were mixed in a round bottle equipped with a stirrer and a reflux condenser. The reaction was carried out at 70°C and sampling was conducted over the reaction time. The solution was separated from the catalyst by using a magnetic bar and analyzed using a gas chromatograph.

Characterization
Particle size measurement was performed by photon correlation spectroscopy (Malvern Instruments Nanosizer ZS). The morphology and diameter were measured by TEM on a Jeol JEM 2100 electron microscope. Infrared spectroscopy (IR) with a spectrometer from Bruker (IFS 66v with Raman module FRA 106, Bruker Optik GmbH, Ettlingen, Germany). The samples were prepared by mixing with KBr and pressing into a compact pellet. TGA was conducted with a TGA 2950 (TA instruments GMBH), under nitrogen atmosphere temperature range between
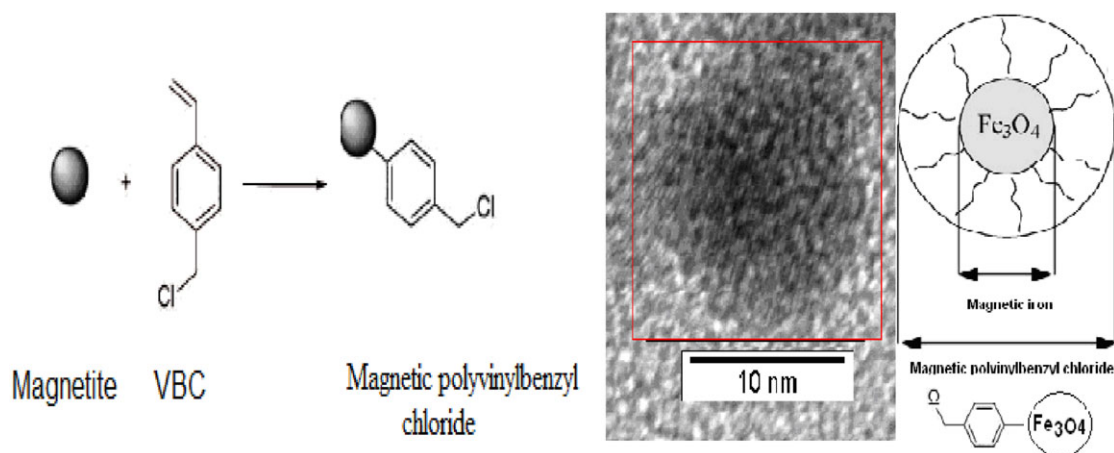
Figure 1. Polymer support of magnetic polyvinylbenzyl chloride nanoparticles.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

30 and 900°C. The concentration of Pt in the samples was measured by AAS using ICP-OES spectro flame argon. The technique makes use of absorption spectrometry to assess the concentration of an analyst in a sample. In general, each wavelength corresponds to only one element. The sample was prepared by acid digestion. Decomposition involves the libration of the metal of interest from an interfering matrix by using acid and external heat source. The concentration of the element in the sample solutions is determined directly by the spectrometer.

GC is a common type of chromatography used in analytic chemistry for separating and analyzing compounds that can be vaporized without experimental decomposition. Gas chromatograph (Shimadzu GC14-A) was equipped with a capillary column and a flame ionization detector. The operating conditions for GC are as follows: initial temperature at 70°C, initial time at 1 min, injected temperature at 200°C, and detector temperature at 280°C. The yield of reduced cinnamaldehyde was measured by GC and calculated by using the internal standard method after catalytic reduction.

RESULTS AND DISCUSSION

Preparation of Polymer Support
Polymers support of magnetic polyvinylbenzyl chloride nanoparticles with and without crosslinker was prepared by using miniemulsion polymerization.[21,22] Reaction takes place by polymerization of VBC and magnetic nanoparticles as shown in Figure 1. The average particles size for polymers support of magnetic polyvinylbenzyl chloride nanoparticles is 10 nm. In Figure 2, the presence of magnetite is characterized by two absorption bands at 632 and 591 cm^{-1}, which correspond to the Fe—O.[24]
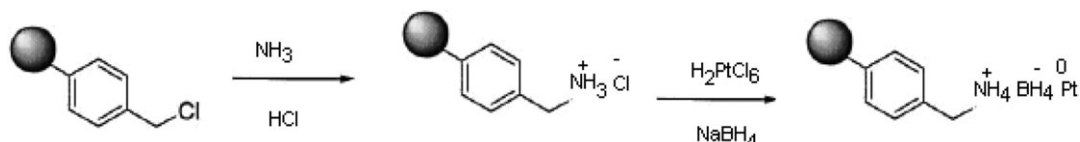
Preparation of Polymer-Supported Pt Catalyst on Magnetite Polyvinylbenzyl Chloride Nanoparticles
The active chlorine group on magnetite polyvinylbenzyl chloride nanoparticles is aminated with ammonia dissolved in organic solvent (toluene) for 6 h, leading to a basic ion exchange resin of magnetite polyvinylbenzyl quaternary salt (ionic form). Then, the Pt precursor H_2PtCl_6 was attached by ion exchange. Finally,
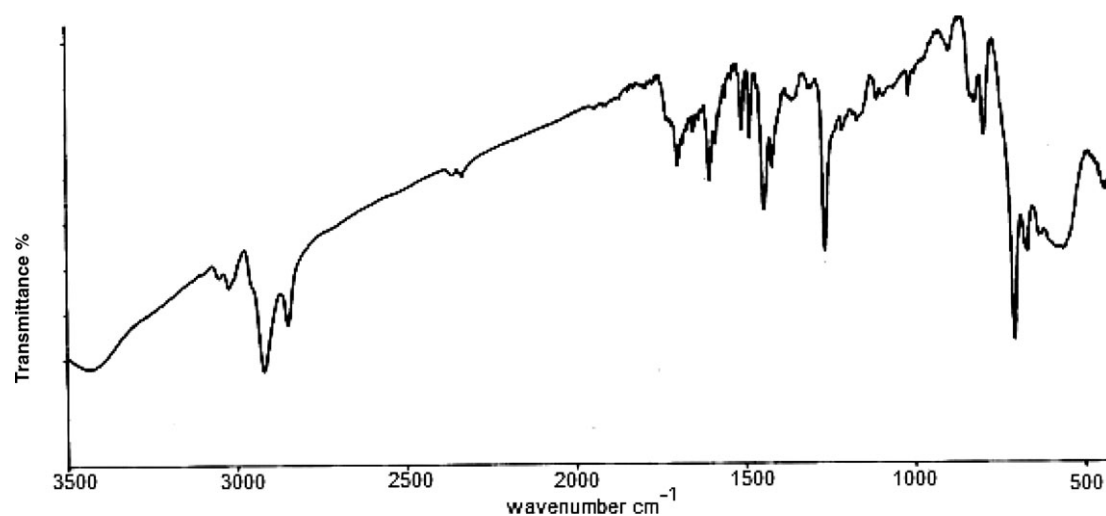
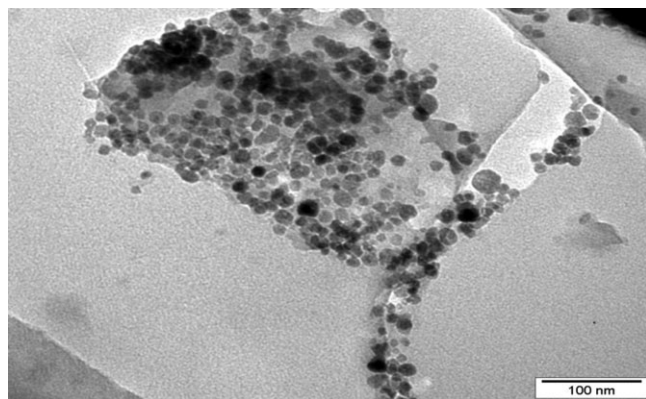**Figure 2.** IR spectrum of magnetite polyvinylbenzyl nanoparticles.

Figure 3. Preparation of polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles.

the Pt ions were reduced to Pt metal by the reducing agent NaBH$_4$ as shown in Figure 3.

Characterization of Magnetite Polyvinylbenzyl Quaternary Salt (Ionic Form)

Transmission Electron Microscopy. The morphology and particle sizes are shown in Figure 4 with the aid of a TEM image for magnetite polyvinylbenzyl quaternary salt (ionic form). Figure 4 shows that the particles size is below 20 nm with some agglomeration owing to the high-surface energy between nanoparticles.
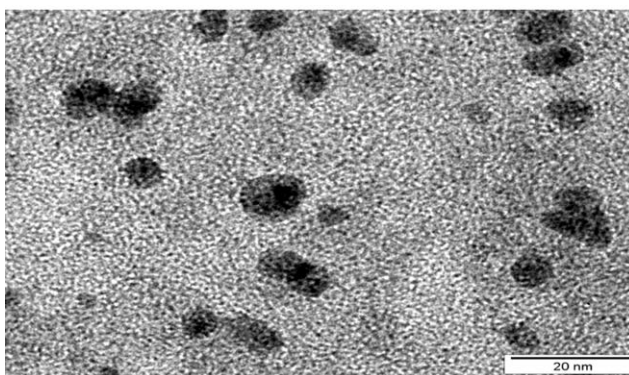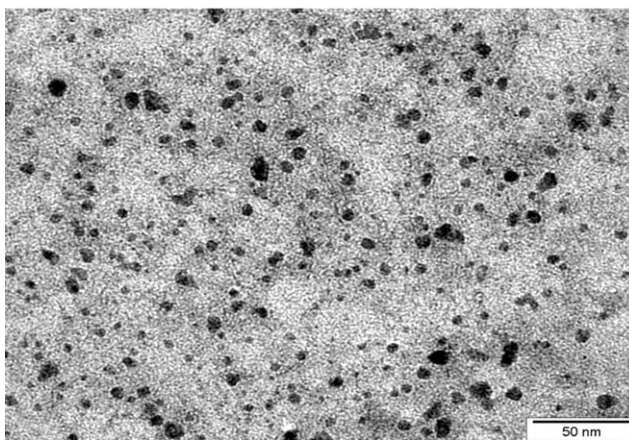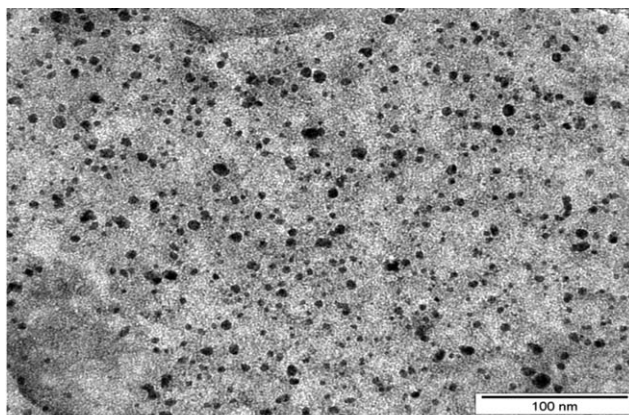

Figure 4. TEM of magnetite polyvinylbenzyl quaternary salt (ionic form).
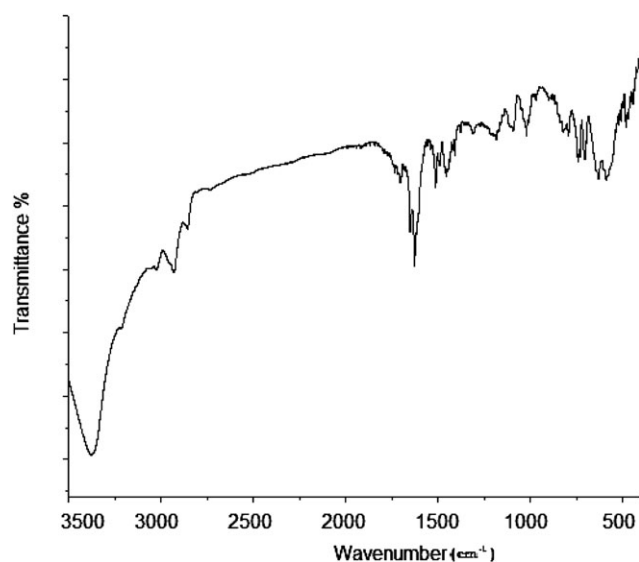

Figure 5. IR spectrum of magnetite polyvinylbenzyl quaternary salt (ionic form).

Infrared. The IR spectrum of magnetite polyvinylbenzyl quaternary salt (ionic form) is shown in Figure 5. The strong absorption bands at 1514 cm^{-1} for the NH$_2$ scissoring (1°-amines), the absorption band at 3350 cm^{-1} for N—H, the absorption band at 1270 cm^{-1} for C—N as well as the absorption band at

Figure 6. low- and high-magnification TEM images of core–shell nanoparticles.
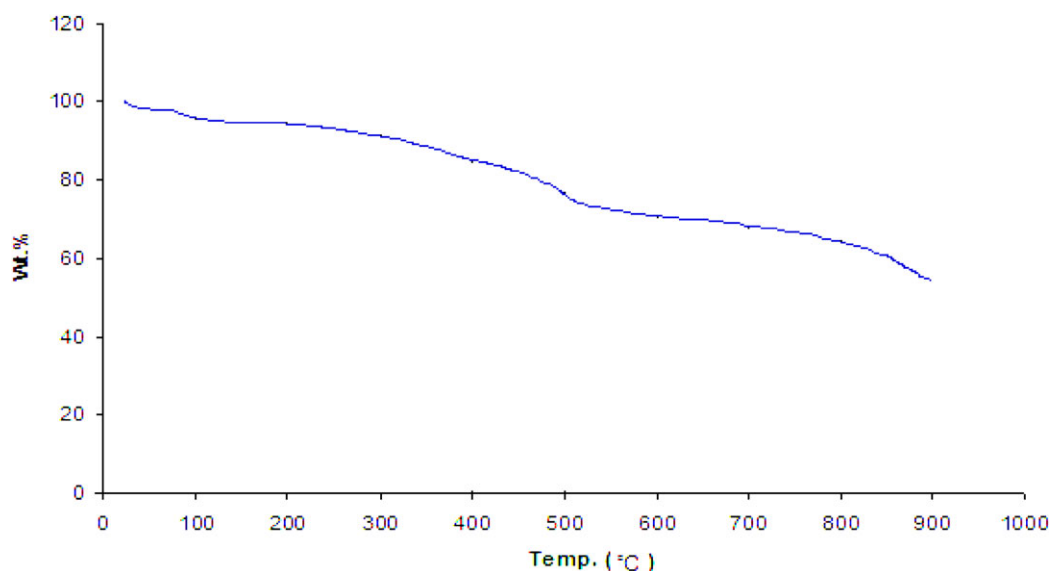
Figure 7. TGA of polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

823 cm^{-1} for NH$_2$ wagging can be seen. The presence of magnetite is illustrated by two absorption bands at 632 and 591 cm^{-1}.[24]

Characterization of Polymer-Supported Pt Catalyst. There is a need for preparing metal nanoparticles having a uniform size and shape. In addition, good dispersion stability for preventing agglomeration of metal nanoparticles in a dispersion medium is another consideration for industrial application. The catalytic materials have magnetic properties which allow separation from the medium after the reaction by magnetic fields. They can be attracted to a magnetic bar in a few seconds.

Transmission Electron Microscopy. In Figure 6, the morphology of polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles is shown in low- and high-magnification TEM pictures.

It can be seen that the particles size is below 20 nm. The nanoparticles are relatively monodispersed and the contrast between

the core and the shell of the nanoparticles was easily distinguishable in TEM images.
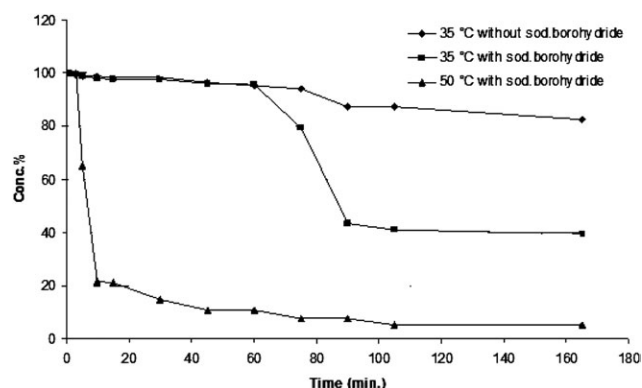
A higher number of particles of polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles is detected compared with magnetite polyvinylbenzyl chloride nanoparticles itself, which is the evidence for insertion of Pt particles in the composite.

Atomic Absorption Spectroscopy. Atomic absorption spectroscopy was used for the determination of Pt metal in the sample. Pt loading in polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles was found to be 17 wt %.

Thermal Gravimetric Analysis. The composition of the hybrid core–shell particles was investigated by means of TGA. TGA gives the mass ratio of thermally decomposable polymeric fraction and inorganic elements. The most volatile and light materials as oleic acid were decomposed first and then followed by the more stable polymer. Figure 7 shows the result for a
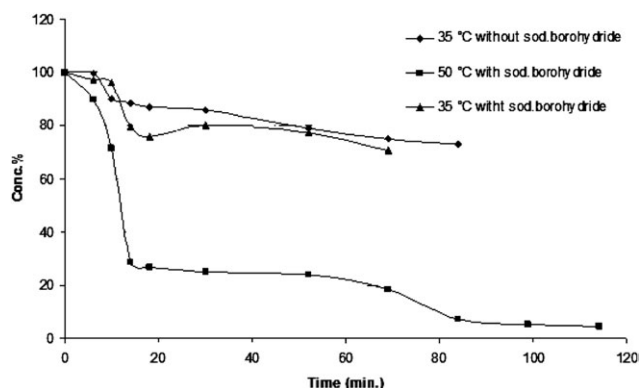
Figure 8. The catalytic activity for polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles in the reduction of cinnamaldehyde.

Figure 9. The catalytic activity for crosslinked polymer-supported Pt-catalyst on magnetite polyvinylbenzyl chloride nanoparticles in the reduction of cinnamaldehyde.

polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles. The sample loses 25% of its weight below 500°C and further 45% till 900°C. The rest of the sample (55%) consists of Pt and Fe.

Catalytic Activity. The obtained material can be dispersed easily as a catalyst and separated after the reaction by magnetic fields. The selective reductions of α,β-unsaturated carbonyl compounds without affecting the carbon–carbon double bond are frequent problems in organic chemistry.[25] The use of basic ion exchange resins loaded with borohydride marks an interesting solution of this problem. The protic solvent (methanol) is necessary as a hydrogen donator for the reduction of cinnamaldehyde.

In Figures 8 and 9, the catalytic activity for both polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles and crosslinked polymer-supported Pt catalyst on magnetite polyvinylbenzyl chloride nanoparticles was measured for the reduction reaction of cinnamaldehyde. The activity of the catalysis was measured as a function on temperature and in the presence of sodium borohydride as reducing agent.

Effect of Temperature. The catalytic activity of the catalysis as function in temperature was measured. With increasing the temperature of reaction from 35 to 50°C, it was found that the reaction rate of the reduction of cinnamaldehyde is increased. Also, a shorter time of the reaction was observed. This is as expected in Figures 8 and 9 in which the faster reduction is not caused by heated methanol at 50°C.

Effect of Addition of Sodium Borohydride. The effect of using sodium borohydride as reducing agent on the catalytic activity of the catalysis is shown in Figures 8 and 9. It was found that without using sodium borohydride the efficiency of reduction for cinnamaldehyde is low and it needs long time to complete the reaction. The solvent (methanol) in this case may act as the reducing agent. The reduction reaction of cinnamaldehyde to cinnamyl alcohol is nearly finished in 15 min.

CONCLUSIONS

A successful implementation for catalysis was achieved by using magnetite polyvinylbenzyl chloride nanoparticles as starting material to prepare an ion exchanger as support for Pt. A 17 wt % Pt-loaded Fe-oxide polyvinylbenzyl chloride nanocomposite was prepared with well-dispersed particles, having an average diameter of 10 nm. The material can be used as a catalyst for organic synthesis which can be separated easily by magnetic forces. The catalytic activity of the catalyst is increased at high temperature (50°C) and the reduction reaction of cinnamaldehyde to cinnamyl alcohol is nearly finished in 15 min.

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