Poly(N-isopropylacrylamide)-Grafted Silica as a Support of Platinum Colloids: Preparation Method, Characterization, and Catalytic Properties in Hydrogenation

KAZUYA SUZUKI,[1] TAKESHI YUMURA,[1] MASAAKI MIZUGUCHI,[2] YUKO TANAKA,[3] CHUN-WEI CHEN,[4] MITSURU AKASHI[4]

[1] Japan Chemical Innovation Institute, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

[2] Suzuki Oil & Fat Co. Ltd., Hyogo 662-0934, Japan

[3] Osaka National Research Institute, Ikeda, Osaka 563-8577, Japan

[4] Department of Applied Chemistry and Chemical Engineering, Kagoshima University, Kagoshima 890-0065, Japan

ABSTRACT: We investigated the composition, properties, and utility of a novel hybrid material of poly(N-isopropylacrylamide)-grafted silica. The modified silica was prepared in two steps: (1) grafting silane layers of active precursors, such as initiator, transfer agent or comonomer onto the silica surface by solution deposition and (2) radical polymerization of N-isopropylacrylamide (NIPAAm) on the grafted silane layers. Thermogravimetric analysis (TGA), elemental analysis (EA), FTIR spectroscopy, and TEM were used to characterize the layer composition, structure, and chemistry, respectively. Well-dispersed platinum colloids have been prepared on the PNIPAAm-grafted silica via the reduction of $PtCl_6^{2-}$ by ethanol. The immobilized Pt colloids were found to be active and stable heterogeneous catalysts for the hydrogenation of ally alcohol in ethanol. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2678–2684, 2000

Key words: silica; graft polymerization; poly(N-isopropylacrylamide); platinum colloids; catalysis

INTRODUCTION

Grafting of polymer on a solid support is a subject of great interest in variety of applications e.g. surface improvement,[1–5] enzyme immobilization,[6] and separation studies.[7,8] In most cases the supports are organic polymers, mainly styrene-divinyl benzene particle or gel-type copolymers. However, these systems suffer from serious disadvantage of lack of thermal, mechanical and chemical stability, which cause the collapse of the support itself. On the other hand, porous silica is well known for its thermal and mechanical stability[9] and used for a solid support of several polymers.[10,11]

Stable noble metal colloids in aqueous solution can be easily and reproducible prepared in a wide range of sizes by different methods.[12] The catalytic properties of noble metal particles depend on the preparation method, the capping agent, and particularly the size and shape.[13] We have reported the formation of platinum nanoparticles in a ethanol-water mixture by ethanol reduction of ionic platinum in the presence of poly(N-isopropylacrylamide) (PNIPAAm).[14] The catalyst exhibited an unusual temperature dependence of activ-

ity owing to the thermoresponsive property of PNIPAAm. Polymer-stabilized noble metal colloids on supports have great potential for environmental and industrial processes.[15,16] In a recent communication, we described the in situ immobilization of well-dispersed platinum colloids on polystyrene microspheres with surface grafted PNIPAAm.[17] These immobilized Pt colloids were found to be active and stable heterogeneous catalysts for the hydrogenation of allyl alcohol in water.

In this work, PNIPAAm-grafted porous silica are used as the support for the platinum colloid immobilization. There are several ways to graft a polymer chain onto a silica surface, e.g. termination of a growing chain on an active group at the surface, copolymerization of an immobilized double bond, and initiation of a polymerization by immobilized initiator.[9] These various anchored compounds are called the active precursors in radical polymerization and all of them can be coupled to the silica surface by solution deposition of functionalized silanes. A two-step preparation route is developed to graft the PNIPAAm to the silica surface. First these active precursors were deposited on the surface of silica, followed by attachment of PNIPAAm by radical graft polymerization. The composition and structure of the resulting silica supports were investigated by Thermogravimetric analysis (TGA), elemental analysis (EA), FTIR spectroscopy, and transmission electron microscopy (TEM). By using the PNIPAAm chains on the surface of silica as the capping agent, well-dispersed platinum colloids were synthesized in situ on the PNIPAAm-grafted silica via ethanol reduction of ionic platinum (Pt-PNIPAAm-Silica). The activity and stability of the immobilized platinum colloids for the hydrogenation of allyl alcohol in ethanol have also investigated.

EXPERIMENTAL

Materials

Porous silica[18] (average particle diameter 4.5 μm, specific surface area 520 m^2 g^{-1}) was obtained from Suzuki Oil & Fat Co. Silane coupling agents of 3-methacryloxypropyltrimethoxysilane (MPS) and 3-aminopropyltriethoxysilane (APS) were purchased from Shin Etsu Chemical Co. and 3-mercaptopropyltrimethoxysilane (MPTS) was purchased from Tokyo Kasei Kogyou Co., Ltd.,

and those silane coupling agents were used without further purification. Toluene, tetrahydrofuran (THF), triethylamine (TEA), benzene, ethanol and 2,2′-azobisisobutyronitrile (AIBN) were of special grades and were purchased from Wako Pure Chemical Industries, Ltd. Ethyl chloroformate, 4,4′-azobis(4-cyanovaleric acid) (ACVA), and chloroplatinic acid (H$_2$PtCl$_6$H$_2$O, special grade) were purchased from Wako Pure Chemical Industries, Ltd., and were used without further purification. N-Isopropylacrylamide (NIPAAm) was donated by Kohjin Co. Ltd., and was recrystallized before use. Platinum-activated carbon (Pt/C, 5% of Pt) was used as received.

Surface Modification of Silica with Silane Coupling Agent

A typical procedure for modifying of the coupling agent (MPS, APS or MPTS) is as follows. Silica (100 g) was first dried at 400°C for 2 h and then placed under a stream of nitrogen in a glass flask equipped with a reflux condenser, together with 850 mL of toluene. APS (150 mL) was then introduced and the solution was stirred at 110°C for 15 h under nitrogen. The surface modified silica was dried at 200°C for 2 h and then washed with methanol and water several times.

Surface Modification of Silica with Radical Initiator

For the reaction between ACVA and APS-modified silica, a 500 mL flask was filled with 373 mL of THF. The flask was then cooled at 0°C. ACVA (7.5 g) was added and then 8.2 mL of ethyl chloroformate and 3.3 mL of TEA were also added. After 15 min, APS-modified silica (20 g) was introduced to the reaction mixture. After 1 h of reaction, the mixture was refrigerated overnight. The precipitated solid was filtered out, washed with THF, water and methanol, and dried under vacuum to give radical initiator-carrying silica.

Graft Polymerization of NIPAAm on Silica

A typical graft polymerization of NIPAAm on silica is as follows. The mixture of ACVA-modified silica (10 g) and NIPAAm (61 g) was stirred in benzene (1.2 L) under nitrogen at 60°C for 48 h. The reaction mixture was discharged into acetone and the resulting solid was filtered out, washed with water and acetone and dried at 60°C overnight.

For determining the molecular weight of PNIPAAm grafted on the surface of silica, the

grafted PNIPAAm could be removed from the surface by stirring it in a 20% solution of hydrogen fluoride for 24 h at 50°C. This procedure breaks down the silica network but leaves the PNIPAAm chains unaltered, as we tested with a free polymer. The ungrafted polymers were washed thoroughly with water and then freeze-dried.

### Preparation of Pt Colloids on PNIPAAm-Modified Silica

$H_2PtCl_6H_2O$ (0.1 mmol Pt) and PNIPAAm modified silica (219 mg, 0.23 mmol as PNIPAAm monomeric unit) were added in an ethanol/water mixed solvent (6/4, v/v, 38 mL), and the solution was then refluxed at 90°C in an oil bath. After an induction period, the color of the mixture changed suddenly from pale yellow to dark gray. The reaction mixture was boiled for 90 min before being allowed cooling. After separating the silica from the reaction mixture by centrifugation (4000 rpm, 10 min) and redispersing them in ethanol, the activity and stability of the Pt colloids on the silica for hydrogenation of allyl alcohol were studied.

Hydrogenation of Allyl Alcohol

Catalytic hydrogenation reaction of allyl alcohol at 25°C under atmospheric pressure were performed as follows: into a 50 mL flat-bottom flask, 15.2 mL Pt-PNIPAAm-silica solution (the amount of platinum metal = 4×10^{-6} mol) was pipetted as well as 2.8 mL of ethanol. The mixture was agitated with a magnetic stirrer at room temperature under 1 atm of hydrogen. After a steady volume of the gas phase was attained, the reaction was initiated with an addition of 2 mL of 1.0 mol/dm^3 ethanol solution of the substrate to the agitated mixture (the final volume of the liquid phase was 20 mL). The hydrogen uptake was monitored by a gas burette during the reaction. A sample was taken 10 min after the addition of the substrate and analyzed by analytical gas chromatography (GC). The amount of 1-propanol was detected and the reaction rate was calculated according to the substrate conversion detected by GC. After each reaction, the catalyst was separated by centrifugation, washed with ethanol, and used for the next run.

Instruments

FTIR-spectra are recorded on a Shimazu LPIR-8200PC by the DRIFT (diffuse reflectance infra-
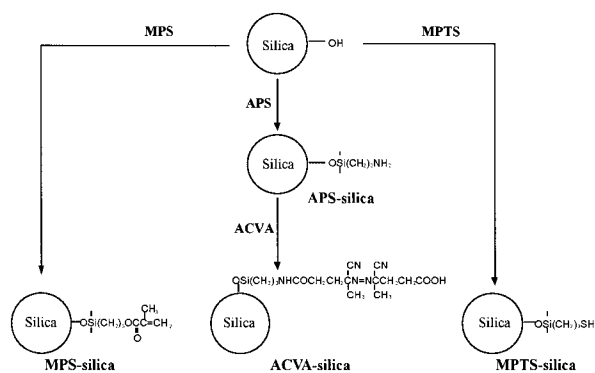

Scheme 1   Schematic presentation of the synthetic routes for the modification of silica.

red Fourier transform) technique. The amount of surface modifier on silica was calculated from weight loss in thermogravimetric analysis (TGA) at 115–640°C using Shimazu thermogravimetric analyzer TGA-50 and elemental analysis using CE instruments EA1110. The molecular weight of PNIPAAm immobilized on silica was determined by means of gel permeation chromatography on a TOSOH GPC-8020 using dimethylformamide (DMF) as eluent and using polystyrene standards. Pore volume and specific surface area of silica were calculated from the amount of nitrogen adsorbed on the surface of silica using nitrogen gas adsorption apparatus Bellsorp 28SA (Bell Japan, Inc.). Transmission Electron Microscopy (TEM) images were obtained with a Hitachi H-700H microscope operation at an acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Surface Modification of Silica and Graft Polymerization

As shown in Scheme 1, silica surface was treated with MPS, APS or MPTS. MPS is used for coupling PNIPAAm by copolymerization initiated by AIBN. In the case of APS a further reaction with active azo compound ACVA is needed to fix a radical initiator and resulting ACVA-modified silica (ACVA-silica) can initiate polymerization of NIPAAm. MPTS serves as a transfer agent in the radical polymerization of NIPAAm initiated by AIBN, and PNIPAAm can be grafted from the sulfur ended radical left on the silica. Scheme 2 shows graft polymerization of NIPAAm onto the surface of ACVA-silica.
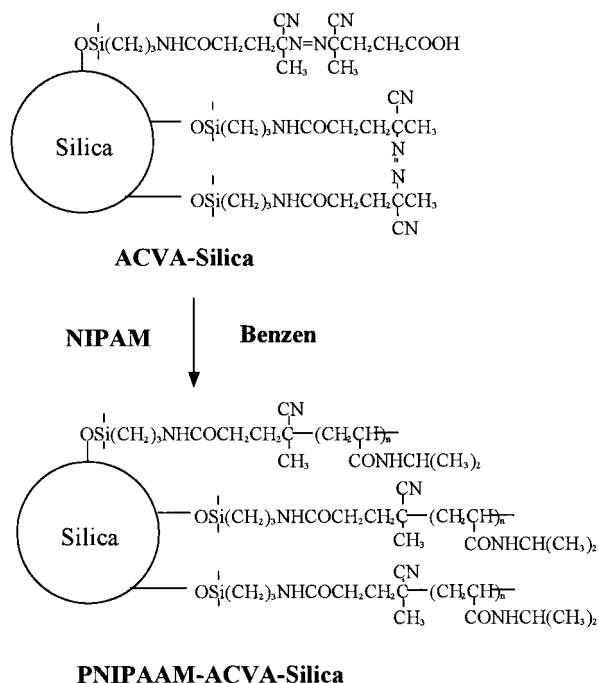
Scheme 2 Schematic of graft polymerization of N-isopropylacrylamide on the ACVA-modified silica.

The yields of the surface modification and graft polymerization were summarized in Table I. The contents of MPS, MPTS, APS, ACVA and PNIPAAm were calculated from the data of TGA weight loss and elemental analysis. The TGA weight loss at 30–115°C is attributed to water adsorbed on the surface of silica. The carbon con-

tent for each modified silica derived from TGA is in a good agreement with that from elemental analysis. It is clear that the largest amount of grafted PNIPAAm was obtained from the ACVA-silica. It is expected that the initiation of polymerization leads to terminally grafted polymers. At the same time, ungrafted PNIPAAm chains can only be produced from the ungrafted ends of the ACVA. Carlier et al. studied the grafting efficiency of vinylbenzyl chloride on MPS, ACVA or MPTS modified silica and found that ACVA-silica had the largest amounts of grafted polymer.[10]

The diffusive reflectance FTIR spectrum for each modification step of PNIPAAm-grafted ACVA-silica (PNIPAAm-ACVA-silica) is shown in Figure 1. APS-modified silica exhibited peak at 2954 cm^{-1} (CH$_2$) in addition to the peaks of original silica. Treatment of ACVA produced new peaks at 1647 cm^{-1} (C=O amide), 1542 cm^{-1} (N—H amide), 1710–1700 cm^{-1} (C=O carboxylic acid), and 2995 cm^{-1} (CH$_3$). After graft polymerization of NIPAAm, the bands characteristic of the PNIPAAm are clearly seen at ca. 2995, 2954, 1647, and 1541 cm^{-1}. These observations provide evidence for the surface modification and graft polymerization on the surface of silica, as illustrated in Scheme 2.

TEM images of the unmodified silica and PNIPAAm-ACVA-silica are shown in Figure 2. The TEM image of PNIPAAm-ACVA-silica showed a uniform layer on the surface of silica, while no layer was observed for the sample of

**Table I   Elemental and Thermal Gravimetric Analyses (EA and TGA) of Various Surface-Modified Silica Samples**

Surface Modifier	None	APS	APS + ACVA	APS + ACVA + PNIPAAm	MPTS	MPTS + PNIPAAm	MPS	MPS + PNIPAAm
EA TCC^a (%)	0.03	3.86	7.64	19.75	5.21	11.03	9.39	14.15
TGA Weight loss (%) at								
30–115°C	4.40	2.40	3.26	2.79	0.61	0.54	0.53	0.93
115–640°C	0.60	8.00	12.65	30.62	9.63	18.50	14.11	21.20
TDOG^b (mg/g-silica)	—	89	150	460	107	229	165	272
Polymer amount (mg/g-silica)	—			310		122		107
TCC^c (%)		5.2	7.8	19.7	4.6	10.5	9.4	13.9

^{a} Total carbon content is measured using elemental analysis.
^{b} Thermally decomposed organic group is calculated from TGA weight loss (%) by eq. of 1000× (weight loss at 115–640°C)/(100-weight loss at 30–640°C).
^{c} Total carbon content is calculated by multiplying the following factor to the organic group: 0.621, 0.585, 0.480, 0.661, 0.636 for APS, ACVA, MPTS, MPS, and PNIPAAm, respectively. The factors mean the weight ratio of carbon in the organic group.
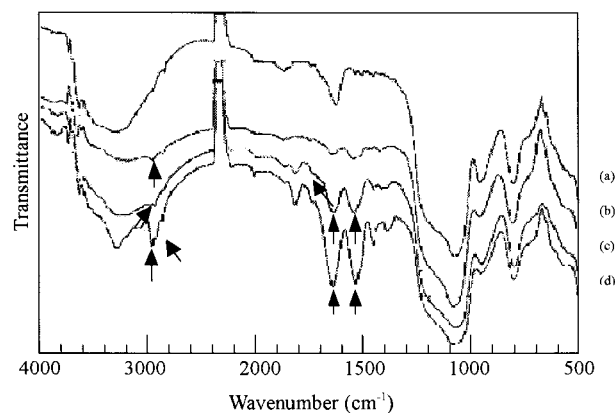
Figure 1 Diffusive reflectance infrared spectra of (a) unmodified, (b) APS-modified, (c) ACVA-modified, (d) PNIPAAm-ACVA-modified silica diluted by KBr.

ether unmodified silica or ACVA-silica. These results indicate that the PNIPAAm was grafted on the silica surface through the polymerization initiated by the azo compound on the surface.

The specific surface area and the pore volume for silica and modified silica were shown in Table II. These data were calculated by the amount of nitrogen adsorbed on the surface of silica or modified silica using Dollimore-Heal method.[19] The amounts of the specific surface area and the pore volume were decreased on modification of APS or ACVA, which demonstrated that the surface of silica was coated a silane layer of APS or ACVA. These values were decreased drastically after graft polymerization of NIPAAm, indicating that NIPAAm was grafted not only on the surface of silica but also inside the pores of silica. Controlling the surface characters of silica by modification makes an important role for its application.[20] We conclude that physical properties, such as surface area and pore volume, can be controlled by chemical modification and adjustment of the amounts of modifier.

The number average molecular weight of PNIPAAm was calculated after removing silica by etching PNIPAAm-ACVA-silica with 20% hydrofluoric acid solution. It was confirmed that such treatment showed no obvious effect on the number average molecular weight of linear PNIPAAm. The number average molecular weight of PNIPAAm grafted on silica was ca. 7.7 $\times 10^4$, estimated by GPC measurement using polystyrene as a standard.

Preparation of Pt Colloids on Silica

By using the surface-grafted PNIPAAm as the capping agent, well-dispersed platinum colloids were generated and immobilized on the surface of silica (Scheme 3). The coordination of metal ions to polymer plays an important role in the production of metal sols by aqueous methanol reduction of metal salts with respect to the nucleation and the controlled growth of the nuclei.[21] The surface-grafted PNIPAAm can coordinate to platinum ions before reduction through the nitrogen atom in the amide group. When initial metal particles are formed, the strong interaction between PNIPAAm and Pt atoms prevents individual colloidal particles from coalescing with each other, thus giving the colloids a smaller average diameter and a higher degree of monodispersity. The detail mechanism of polymer-protected platinum nanoparticles in an ethanol-water mixture was described in our previous paper.[14]

The immobilized Pt colloids on PNIPAAm-ACVA-silica (Pt-PNIPAAm-ACVA-silica) can be easily separated from the reaction mixture by centrifugation and the supernatant was colorless. The PNIPAAm branches not only stabilize the platinum colloids by steric repulsion, but also immobilize them on silica. TEM images of the Pt-PNIPAAm-ACVA-silica are shown in Figure 3. Figure 3(a) and (b) show a lateral view and the surface of the Pt-PNIPAAm-ACVA-silica, respectively. It was clearly found that Pt colloids were adsorbed onto the PNIPAAm-ACVA-silica in a well-dispersed way.

(a) Unmodified silica

1 μm

(b) PNIPAAm-ACVA-silica

1 μm
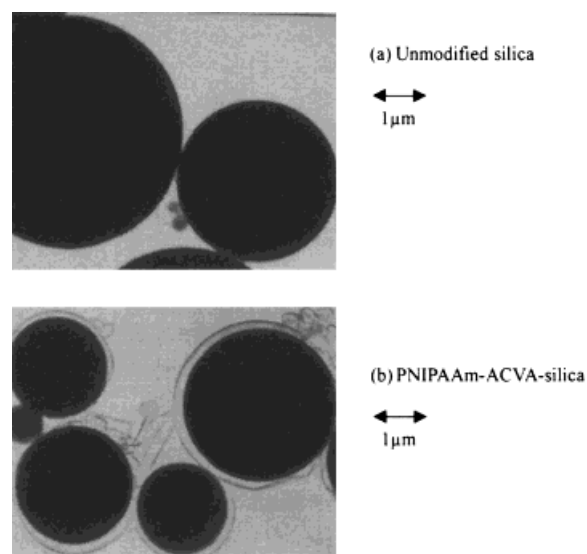
Figure 2 Transmission electron micrographs of (a) unmodified silica and (b) PNIPAAm-ACVA-modified silica.

Table II   Specific Surface Area and Pore Volume for Various Surface-Modified Silica Samples[a]

Surface Modifier	None	APS	APS + ACVA	APS + ACVA + PNIPAAm
Specific surface area (m^2/g)	522	338	222	11
Pore volume (mm^3/g)	654	409	252	13

[a] Measured by the amount of nitrogen adsorbed on the surface and calculated by Dollimore-Heal method.[18]

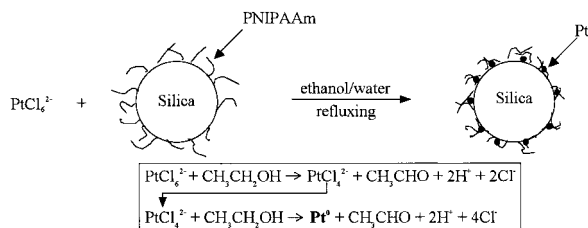### Catalytic Properties of Immobilized Pt Colloids in Hydrogenation

The platinum colloid on the synthesized PNIPAAm-ACVA-silica was employed as a heterogeneous catalyst for the hydrogenation of allyl alcohol in ethanol in comparison with Pt colloid on unmodified silica (Pt-silica) or commercial platinum-activated carbon (Pt/C). The data in Figure 4 show the initial hydrogenation rate, with the same sample of catalyst recycled five times. The Pt-PNIPAAm-ACVA-silica catalyst showed higher hydrogenation activity than the catalysts of Pt-silica and Pt/C. The catalyst also retained high activity in the hydrogenation on recycling five times, though a small decrease in activity was observed after the first catalytic run. The commercial catalyst, Pt/C, was not precipitated on centrifugation (4000 rpm, 10 min); therefore, it is hard to be reused after one catalytic run. Since Pt colloids that adsorbed on the modified silica have very weak affinity to the support, the desorption of Pt colloids from silica surface occurs. As a result, the Pt-silica catalyst displayed rather rapid deactivation on recycling in the hydrogenation. As for Pt-PNIPAAm-ACVA-silica, the Pt colloids have adsorbed in a controlled, well-dispersed manner on the support owing to the strong affinity between PNIPAAm and Pt colloid. The coalescence of a proportion of the smallest particles may contribute to the small decrease in activity after one recycle in hydrogenation.
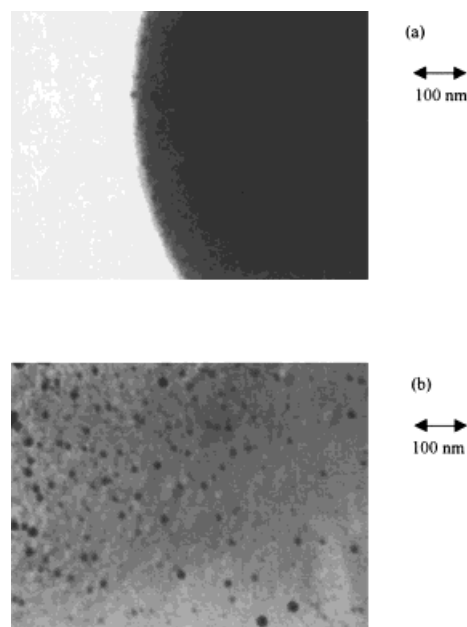
We have already evaluated the thermosensitive properties of PNIPAAm-stabilized platinum sol and found that the activity for the hydrogenation of allyl alcohol in water can be regulated through a temperature change.[14] Ongoing research in our group suggests that the activity of Pt-PNIPAAm-ACVA-silica also must be moderated through a temperature change for catalytic reactions in water.

CONCLUSIONS

Rather large amounts of poly(N-isopropylacrylamide) were grafted by radical polymerization

Figure 3   Transmission electron micrographs of platinum colloids immobilized on PNIPAAm-ACVA-silica: (a) The lateral view, and (b) the surface of Pt-PNIPAAm-ACVA-silica.

$$PtCl_6^{2-} + CH_3CH_2OH \rightarrow PtCl_4^{2-} + CH_3CHO + 2H^+ + 2Cl^-$$

$$PtCl_4^{2-} + CH_3CH_2OH \rightarrow Pt^0 + CH_3CHO + 2H^+ + 4Cl^-$$

Scheme 3   Schematic representation of the immobilization of platinum colloids on PNIPAAm-grafted silica.
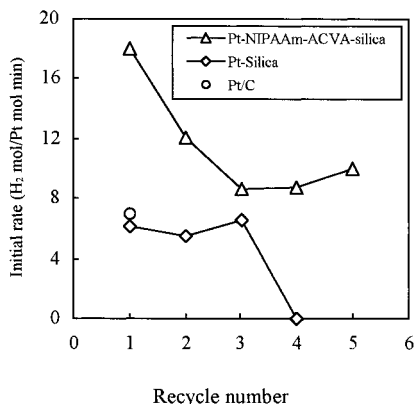
Figure 4 Catalytic activity and stability of platinum colloids on PNIPAAm-ACVA-silica and unmodified silica in the hydrogenation of allyl alcohol. Conditions: catalyst, Pt, 0.004 mmol; allyl alcohol/Pt = 500; solvent, ethanol, 20 mL; 25°C; Hydrogen, 1 atm.

onto the surface of silica that was modified by a silane layer of initiator, transfer agent and comonomer, respectively. The highest amount of grafted PNIPAAm was obtained by using an azo initiator bound to the surface. FTIR and TEM studies confirmed the graft polymerization of N-isopropylacrylamide on the surface of azo initiator-modified silica.

Well-dispersed platinum colloids could be synthesized in situ on the surface of PNIPAAm-grafted silica via ethanol reduction of $PtCl_6^{-2}$. The platinum colloids on PNIPAAm-ACVA-silica showed a strong catalytic activity and could be recyclable after centrifugation.

The immobilized platinum colloids also have a great advantage over these on a polymeric support; that is, they are loaded on silica (an inorganic support) which has thermal and mechanical stability. Due to this promising combination of the properties of inorganic support with these of metal colloids, we might expect some interesting developments of the hybrid material.

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