Cross-linked polymer coated Pd nanocatalysts on SiO₂ support: very selective and stable catalysts for hydrogenation in supercritical CO₂

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Using greener solvents, enhancing the selectivity and stability of catalysts is an important aspect of green chemistry. In this work, we developed a route to immobilize Pd nanoparticles on the surface of silica particles with cross-linked polystyrene coating by one-step copolymerization, and Pd(0) nanocatalysts supported on the silica particle supports with cross-linked polystyrene coating were successfully prepared. The catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), plasma optical emission spectroscopy, and thermogravimetric analysis (TGA), and were used for hydrogenation of 2,4-dimethyl-1,3-pentadiene to produce 2,4-dimethyl-2-pentene and allyl alcohol to produce 1-propanol. It was found that the selectivity of the reaction was enhanced significantly by the polymer coating, and the catalysts were very stable due to the insoluble nature of the cross-linked polymers. Supercritical (sc)CO₂ can accelerate the reaction rates of the reactions catalyzed by the specially designed catalysts significantly. The excellent combination of polymer coating and scCO₂ has wide potential applications in catalysis.

Introduction

It is known that metal nanoparticles are highly active and selective catalysts for many reactions. However, the naked nanoparticles aggregate easily, resulting in a decrease in catalytic activity and selectivity. To solve this problem, metal nanocatalysts have been immobilized using different supports such as carbon, metal oxides, molecular sieves,¹ and polymers.² Some functional polymers have also been used to stabilize metal nanocatalysts. For example, Jiang and Gao prepared heterogeneous Pd(0) nanoparticle catalysts by encapsulating the nanocatalysts in polyamidoamine dendrimers on SBA-15.³ The organic-inorganic hybrid composites showed highly catalytic activity and selectivity for the hydrogenation of allyl alcohol. Bruening and coworkers embedded Pd nanoparticles in multilayer polyelectrolyte films around alumina particles, which were prepared by the layer-by-layer deposition method.⁴ The supported catalysts were used to catalyze hydrogenation of allyl alcohol, 1-penten-3-ol and 3-methyl-1-penten-3-ol, which differ only in the substituents at the α -carbon of the double bond, and it was demonstrated that the polyelectrolytes limited aggregation of the metal nanoparticles, and reaction rates of the alcohols were very different due to restricting access to active sites of the branched alcohols.

Hydrogenation is among the most important processes in the chemical industry. In many cases it is very important to control the selectivity of hydrogenation reactions.^{3,4} The design and preparation of special catalytic materials with steric effects is an effective way to do this.⁵ It is known that cross-linked polymers

are not soluble in ordinary solvents or reaction substrates. Therefore, the nanocatalysts on the particle supports with a cross-linked polymer coating should be very stable, and the polymer coating may restrict access of some active bonds to the active sites of the catalysts, and improve the selectivity of the reactions with multiple active bonds. However, how to coat nanocatalysts on particle supports with cross-linked polymer films is challenging. Besides, the coating should reduce the reaction rate of reactions. Therefore, acceleration of the reaction rate for the reactions catalyzed by this kind of specially designed catalyst is also important.

It is known that supercritical $(sc)CO_2$ is a cleaner solvent and a promising alternative to organic solvents. The interfacial tension of $scCO_2$ is zero and its diffusivity is much larger than liquids, which can enhance the rates of many reactions.⁶ Therefore, it is possible to increase the reaction rate of the polymer-coated metal nanoparticles using $scCO_2$.

In this work, we developed a route to immobilize Pd nanoparticles on the surface of silica particles with crosslinked polystyrene coating by one-step copolymerization. The supported Pd catalysts were used to catalyze the hydrogenation of 2,4-dimethyl-1,3-pentadiene and allyl alcohol (Scheme 1). It was found that the selectivity of the reaction was enhanced



pentadiene and allyl alcohol.

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significantly by the polymer coating, and the catalysts were very stable due to the insoluble nature of the cross-linked polymers. As far as we know, this is the first work to coat the nanocatalysts on particle supports with cross-linked polymers. This method can be potentially used to prepare the cross-linked polymer-coated nanocatalysts of some other metals. Our work demonstrated that supercritical (sc)CO₂ can accelerate the reaction rates significantly. We believe that the idea to combine cross-linked polymer-coated nanocatalysts on supports and scCO₂ can be applied to enhance the selectivity of many reactions with two or more active bonds effectively.

Results and discussion

Synthesis of the polymer-coated catalyst

Scheme 2 shows the route to fabricate the cross-linked polystyrene-coated catalysts. The detailed procedures to prepare the catalysts are described in the Experimental section, and the chemical structures of styrene (St), divinylbenzene (DVB), potassium persulfate (KPS), 3-aminopropyltriethoxysilane (APS), poly(*N*-vinyl pyrrolidone) (PVP), sodium styrene sulfonate (NaSS) and allylamine (AA) are given in Scheme 3. The monodispersed SiO₂ particles with the average size of about 230 nm were prepared by the method in the literature.⁷



Scheme 2 General scheme of synthesis of polystyrene-coated Pd(0) nanoparticles on the surface of SiO_2 .

Fig. 1 shows FTIR spectra of pure SiO₂ and aminofunctionalized SiO₂ particles. The bands at 3425 and 1630 cm⁻¹ are attributed to the stretching and bending vibrations of water molecules adsorbed on the surface of SiO₂. After the functionalization of SiO₂ with APS, the intensity of the band at 967 cm⁻¹ (Si-OH bending vibration peak) obviously decreases and a new band appears at 2980 cm⁻¹ due to C-H stretching vibration, suggesting that SiO₂ particles were functionalized by APS.⁸ Pd²⁺ ions were then anchored onto the surface of aminofunctionalized SiO₂ particles. The Pd²⁺ on the functionalized-SiO₂ particles was reduced by H₂ at 150 °C for 5 hours to obtain dark brown Pd(0)-SiO₂ particles (catalyst A), as shown in the TEM image in Fig. 2a. It can be seen that Pd(0) nanoparticles with the size of 2–5 nm were uniformly decorated on the surface



Divinylbenzene (DVB) Styrene (St) Sodium Styrene Sulfonate (NaSS)

$$\begin{array}{ccc} O & O \\ I & I \\ K-O-S-O-O-S-O-K \\ I & I \\ O & O \end{array}$$

Potassium Persulfate (KPS)

CH₂=CHCH₂NH₂

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Allylamine (AA)
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$$\langle N \rangle_{O}$$

 \downarrow
 \downarrow
 $CH-CH_2$
 \downarrow
 n

3-aminopropyltriethoxysilane (APS)

Poly(N-vinyl pyrrolidone) (PVP)

Scheme 3 The chemical structures of some chemicals used.



Fig. 1 FTIR spectra of (a) original SiO_2 , (b) amino-functionalized SiO_2 , (c) catalyst B and (d) catalyst C. The inset shows magnified FTIR spectra.



Fig. 2 TEM images of (a) catalyst A without the polymer coating, (b) catalyst A after used 4 times, (c) catalyst B with incomplete polystyrene coating, (d) catalyst C with complete polystyrene coating, (e) catalyst C after used 4 times. The inserts of (b), (c), and (d) are corresponding SEM images.

of SiO₂ particles. Coating of the cross-linked polystyrene on the catalyst A was achieved by emulsion polymerization using St as the monomer, DVB as a crosslinker, PVP as a stabilizer, KPS as an initiator, NaSS as an emulsifier and AA as a copolymeric monomer. It can be observed that incomplete polystyrene coating was formed without the addition of AA (Fig. 2c), while complete coating was formed with the addition of AA (Fig. 2d). The reason may be that the surface of SiO₂ was functionalized by APS containing richly cationic amines.9 On the other hand, polystyrene particles prepared by emulsion polymerization using KPS as an initiator and NaSS as an emulsifier exhibited a negatively charged surface.¹⁰ Without addition of AA, incomplete polystyrene coating on Pd(0) nanoparticles (catalyst B) was therefore formed by electrostatic adsorption of polystyrene particles on the surface of SiO₂ particles. In the presence of AA, however, AA firstly interacted with Pd nanoparticles on the surface of SiO₂ particles by means of terminal amines of AA, and then copolymerized with monomer St via a C=C double bond of AA, resulting in the formation of complete polystyrene coating on Pd(0) nanoparticles (catalyst C) with the average thickness of polystyrene coating about 25 nm, which was estimated from the diameters of the coated and uncoated particles. This indicates that the existence of AA can greatly affect the morphology of polystyrene coating. FTIR spectra of catalysts B and C (Fig. 1, Spectra c and d) further confirm the presence of the cross-linked polystyrene on the surface of SiO₂ particles according to the typical absorption bands of polystyrene at 1452, 1492, 2928 and 3028 cm⁻¹.¹¹ The contents of Pd(0) in catalyst A, B and C were 0.47%, 0.35% and 0.28%, respectively, which was determined by inductively coupled plasma optical emission spectroscopy (ICP-AES, Vista-MPX).

Fig. 3 shows the TGA results of catalyst B and catalyst C. The major weight losses occurred in the temperature range from 250



Fig. 3 Thermogravimetric curves for catalyst B (a) and catalyst C (b).

to 500 °C because of the thermal decomposition of polystyrene. The final weights (assumed to be Pd(0)-SiO₂) were 81.4 and 69.5% for catalysts B and C, respectively. This indicates that the content of polystyrene in catalyst C was higher than that in catalyst B. The two-step decomposition of catalyst C may result from the existence of AA in the polymer films. The thickness of catalyst C calculated from the densities and mass percents of the silica and polystyrene in the catalyst was about 24 nm, which agrees with that estimated from the diameters of the coated and uncoated catalyst particles.

Hydrogenation reactions

We studied the hydrogenation of 2,4-dimethyl-1,3-pentadiene and allyl alcohol (Scheme 1) using the three catalysts, and the results are listed in Tables 1 and 2, respectively. The naked Pd(0)nanoparticles in catalyst A were much more active than the polymer-coated Pd(0) nanoparticles in catalyst B and catalyst C. This is easy to understand because the polymer coating

Table 1 The conversion, selectivity and turnover frequency (TOF) of hydrogenation of 2,4-dimethyl-1,3-pentadiene using different catalysts at $40 \,^{\circ}C^{a}$

Entry	Catalyst	P _{CO2} [MPa]	Time [h]	Conversion [%]	TOF ^b	Selectivity [%]		
						2,4-dimethyl-2- pentene	2,4-dimethyl-1- pentene	2,4-dimethyl- pentane
1	А	0	0.2	>99.7	28000	51.2	48.4	0.4
1-1 ^c	А	0	0.3	>99.7	18667	51.5	48.2	0.3
1-2 ^c	А	0	0.5	>99.7	14000	51.1	48.3	0.6
1-3 ^c	А	0	0.7	>99.7	8000	51.2	48.5	0.3
$1-4^{c}$	А	0	1.0	>99.7	5600	51.3	48.2	0.5
2	В	0	2.5	>99.7	2604	65.0	34.5	0.5
3	С	0	99.0	>99.7	57	75.2	24.5	0.2
4	С	2	16.0	27.5	96	75.5	24.4	0.1
5	С	5	16.0	54.8	192	77.2	22.7	0.1
6	С	8	16.0	>99.7	350	80.1	19.8	0.1
6-1 ^d	С	8	16.0	>99.7	350	80.2	19.6	0.2
6-2 ^d	С	8	16.0	>99.7	350	79.9	20.0	0.1
6-3 ^d	С	8	16.0	>99.7	350	80.0	19.9	0.1
6-4 ^d	С	8	16.0	>99.7	350	79.5	20.4	0.1
7	С	11	16.0	86.2	302	77.1	22.8	0.1
8	С	14	16.0	79.1	277	77.0	22.9	0.1
9	Pd/C^{e}	0	0.25	>99.7	22400	50.5	48.9	0.6

^{*a*} Reaction conditions: H₂, 3.0 MPa; the molar ratio of 2,4-dimethyl-1,3-pentadiene to Pd(0) is 5600. ^{*b*} The turnover frequencies (TOFs) are moles of reacted substrate per mole of Pd(0) per hour. ^{*c*} Hydrogenation reaction over catalyst A after being used 4 times. ^{*d*} Hydrogenation reaction over catalyst C after being used 4 times. ^{*e*} Commercial Pd/C with 5% Pd on carbon powder from Baoji Rock Co. Ltd, China.

Table 2 The conversion, selectivity, and turnover frequency (TOF) of hydrogenation of allyl alcohol using different catalysts at 40 °C ^a

Entry	Catalyst	P _{CO2} [MPa]	Time [h]	Conversion [%]	TOF ^b	Selectivity [%] ^c
1	А	0	1.0	>99.7	7500	75.3
$1 - 1^{d}$	А	0	1.1	>99.7	6818	75.6
1-2d	А	0	1.2	>99.7	6250	75.4
1-3 ^d	А	0	1.3	>99.7	5769	75.3
$1-4^{d}$	А	0	1.5	>99.7	5000	75.7
2	В	0	5.0	>99.7	1500	83.1
3	В	8	3.5	>99.7	2140	86.4
4	С	0	9.0	>99.7	833	92.4
5	Ċ	8	5.0	>99.7	1500	93.1
5-1 ^e	Ċ	8	5.0	>99.7	1500	92.9
5-2 ^e	Ċ	8	5.0	>99.7	1500	93.0
5-3e	C	8	5.0	>99.7	1500	92.6
5–4 ^e	С	8	5.0	>99.7	1500	92.4
6	Pd/C ^f	0	1.5	>99.7	5000	74.0

^{*a*} Reaction conditions: H₂, 2.0 MPa, the molar ratio of allyl alcohol to Pd(0) is 7500. ^{*b*} The turnover frequencies (TOFs) are moles of reacted substrate per mol of Pd(0) per hour. ^{*c*} The selectivity to 1-propanol (product). ^{*d*} Hydrogenation reaction over catalyst A after being used 4 times. ^{*f*} Hydrogenation over Catalyst C after being used 4 times. ^{*f*} Commercial Pd/C, 5% Pd on carbon powder from Baoji Rock Co. Ltd, China.

restricts the access of the reactants to the active sites of the catalysts. At the same time, this provides further evidence that Pd nanocatalysts were coated by the polymer.

Table 1 shows that the selectivity of the reaction to the two products, 2,4-dimethyl-1-pentene and 2,4-dimethyl-2-pentene, was nearly the same when catalyst A was used (entry 1), while the selectivity to 2,4-dimethyl-2-pentene was much higher than that to 2,4-dimethyl-1-pentene when catalyst C was used (entry 3). For catalyst A, the two double bonds of the pentadiene with similar activity have similar opportunity to contact the naked Pd(0) nanoparticles on SiO₂ particles, leading to approximately the same selectivity for the two pentenes. For catalyst C, however, the selectivity to 2,4-dimethyl-2-pentene was 75.2%, which is much higher than that catalyzed by silica-supported PAMAM-Pd complexes with 2,4-dimethyl-2-pentene selectivity of 59.0%.5c In other words, more terminal double bonds were hydrogenated. This is understandable because the reactant is a linear molecule, it prefers to approach the Pd particles perpendicularly through the coating surface. Therefore, the terminal double bond has more opportunity for access to Pd(0) nanoparticles than the internal double bond. As catalyst B was used, the selectivities to 2,4-dimethyl-2-pentene and 2,4-dimethyl-1-pentene lie between those of catalyst A and catalyst C because of the incomplete coating (entry 2).

In this work, we also studied the reaction in $scCO_2$ catalyzed by catalyst C because it was the most selective. The results at different pressures are also listed in Table 1 (from entry 3 to entry 8). Obviously, $scCO_2$ can enhance the reaction rate significantly. Moreover, under $scCO_2$ conditions, the selectivity to 2,4-dimethyl-2-pentene can reach 80.1% using catalyst C (entry 6), which is higher than that under solvent-free conditions (entry 3). This may result from the higher diffusivity of the molecules in $scCO_2$. After the hydrogenation of the terminal double bond, the product diffuses out more quickly than the case without $scCO_2$.

The selectivity at different conversions using catalysts A and C are shown in Fig. 4. It can be seen that for the two catalysts used the selectivities to 2,4-dimethyl-2-pentene and 2,4-dimethyl-1-pentene are almost constant with increasing conversion. It is



Fig. 4 The selectivity of products *versus* conversion of 2,4-dimethyl-1,3pentadiene over catalyst A under solvent-free conditions (a), catalyst C under solvent-free conditions (b), and catalyst C under scCO₂ (8.5 MPa) condition (c). (\blacksquare) 2,4-dimethylpentane; (\spadesuit) 2,4-dimethyl-1-pentene; (\blacktriangle) 2,4-dimethyl-2-pentene. Reaction conditions: H₂ 3.0 MPa, temperature 40 °C, the molar ratio of substrate and Pd(0) was 5600.

also worth noticing that the formation of pentane is almost negligible prior to complete consumption of the pentadiene for both catalyst A and catalyst C.

For the hydrogenation of allyl alcohol to produce 1-propanol in Table 2, the selectivity was also greatly improved by the polymer coating on Pd(0) nanoparticles. Especially, the selectivity to 1-propanol approached 92.4% when catalyst C was used (entry 4), which was much higher than that of catalyst

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A (75.3%, entry 1) and commercial Pd/C (74.0%, entry 6), suggesting that the selectivity to 1-propanol was enhanced by the polystyrene coating. The mechanism to enhance the selectivity of this reaction is different from that of the hydrogenation of 2,4dimethyl-1,3-pentadiene. During hydrogenation of allyl alcohol performed with Pd(0) nanoparticles, allyl alcohol also easily isomerizes into byproduct propanal or acetone.3,4,12 As catalyst C was used, the polymer coating in the catalysts suppressed isomerization of allyl alcohol during hydrogenation because it modified both the environment of active sites and access to these active sites, similar to the function of dendrimers³ and polyelectrolyte multilayers⁴ The reaction catalyzed by catalyst C was also conducted in scCO₂. As can be seen in Table 2, the activity of catalyst C under $scCO_2$ condition (entry 5) is much higher than in the absence of CO_2 (entry 4), which further demonstrated that scCO₂ can accelerate the reaction rates significantly. The main reason for this is that scCO₂ has high diffusion and low viscosity, which is favourable to the mass transfer of the reactant and the product.

Reusability of the catalysts

The recyclability of catalysts A and C was tested in this work. After each cycle, the catalyst was reused after washing with ethanol and drying. The results are also presented in Table 1 (entries 1-1, 1-2, 1-3 and 1-4 for catalyst A and entries 6-1, 6-2, 6-3 and 6-4 for catalyst C) and Table 2 (entries 1-1, 1-2, 1-3 and 1-4 for catalyst A and entries 5-1, 5-2, 5-3 and 5-4 for catalyst C). Clearly, the reduction in activity and selectivity of catalyst C was negligible after being reused 4 times, while the activity of catalyst A reduced significantly. The reason is that the stable polymer coating can protect the Pd nanoparticles from aggregation and falling off the support. Figs. 2b and 2e show the TEM images of catalyst A and catalyst C after being used 4 times for hydrogenation of 2,4-dimethyl-1,3-pentadiene, respectively. Apparently, the number of Pd particles of the used catalyst A is much less than that of the original one, as can be seen from Figs. 1a and 1b. However, the morphology of catalyst C was not changed noticeably after being used 4 times (Fig. 2e, the Pd particles cannot be seen because of the coating), providing further evidence for the excellent stability.

Conclusions

In summary, Pd(0) nanocatalysts on a silica support with a cross-linked polystyrene coating were successfully prepared. Highly selective hydrogenation of 2,4-dimethyl-1,3-pentadiene to 2,4-dimethyl-2-pentene and allyl alcohol to 1-propanol can be achieved using the catalysts fabricated, and the catalysts are very stable. The polymer coating provides a steric effect for the high selectivity of the reactions and enhances the stability of the catalysts. scCO₂ can accelerate the reaction rates considerably. We believe that this method can also be used to prepare some other nanocatalysts on the particle supports with a very stable polymer coating, and this class of catalysts may also be used to enhance the selectivity of some other reactions with more than one active chemical bond of similar activity, where high selectivity is difficult to reach by other catalysts.

Experimental

Tetraethyl orthosilicate (TEOS) from Beijing Beihua Fine Chemical Company was distilled prior to use. Aqueous NH₃ solution with a NH₃ content of 25% was supplied by Beijing Yili Fine Chemical Company. 3-Aminopropyltriethoxysilane (APS, analytical grade) provided by Beijing Shenda Fine Chemical Company was used as received. Potassium persulfate (KPS), allylamine (AA), poly(N-vinyl pyrrolidone) (PVP), sodium styrene sulfonate (NaSS) and palladium chloride (PdCl₂) were all analytical grade and purchased from the Beijing Chemical Reagent Company. Styrene (St, analytical grade) from Beijing Chemical Reagent Company and divinylbenzene (DVB) from Tokyo Kasei Kogyo Company were distilled under reduced pressure before use. 2,4-Dimethyl-1,3-pentadiene and allyl alcohol were provided by Aldrich. Hydrogen (99.99%) and CO₂ (99.995%) were supplied by the Beijing Analytical Instrument Factory.

Preparation of SiO₂ particles

The monodisperse SiO₂ particles were synthesized according to the well-known Stöber method.⁷ Typically, the ethanol solution of TEOS was quickly added into the other ethanol solution of NH₃ and H₂O in a 500 mL Erlenmeyer flask. The molar ratio of NH₃:H₂O:TEOS was 1:11:0.22 in the final gel mixture that was stirred at 30 °C for 4 hours. The resulting SiO₂ particles were centrifugally separated from the suspension, ultrasonically washed with ethanol three times, and finally dried at 100 °C.

Preparation of amino-functionalized SiO₂ particles

The monodisperse SiO₂ particles were functionalized with APS.⁸ In a typical experiment, SiO₂ particles (1 g) and APS (1.2 g) were added into a round-bottomed flask containing 15 mL of toluene. After the mixture was stirred under refluxing at 110 °C for 24 hours, the obtained amino-functionalized SiO₂ particles were centrifuged, washed three times with toluene and twice with ethanol, respectively, and dried in air at 100 °C.

Preparation of Pd(0) nanoparticles on amino-functionalized SiO_2 particles

Amino-functionalized SiO₂ particles (1.2 g) were ultrasonically dispersed with 40 mL of water in a 100 mL round-bottomed flask, followed by the addition of 32 mL of PdCl₂ acidic solution (2 mmol L⁻¹, pH = 3). The mixture was stirred with a magnetic stirrer at room temperature for 30 min. Pd²⁺ ions formed a complex with the amine group on the surface of amino-functionalized SiO₂ particles. Separated centrifugally from the suspension and washed ultrasonically with deionized water, Pd²⁺-adsorbed-amino-functionalized-SiO₂ particles were obtained and dried in air at 100 °C for 4 hours. The dried Pd²⁺adsorbed-amino-functionalized-SiO₂ particles were reduced using H₂ (3 MPa) at 150 °C for 5 hours in a 6 mL high-pressure stainless steel reactor, leading to the formation of dark brown Pd(0)-SiO₂ particles.

Preparation of polymer-coated Pd nanoparticles on APS-functionalized SiO₂ particles

The dark brown Pd(0)-SiO₂ particles (0.3 g) were ultrasonically dispersed with 35 mL of water in a 250 mL round-bottomed flask equipped with a condenser. Allylamine (AA, 0.25 mL) and poly(*N*-vinyl pyrrolidone) (PVP, 0.5 g) were added into the flask and agitated with a magnetic stirrer at room temperature for 1 hour. Then, 0.25 g of sodium styrene sulfonate (NaSS), 0.15 g of potassium persulfate (KPS) and 40 mL of water were added into the flask and allowed to mix for 30 min. 2 mL of styrene (St) and 0.2 mL of divinylbenzene (DVB) were then added. Finally, the polymerization was carried out in a nitrogen atmosphere under stirring at 80 °C for 12 hours. The resulting polystyrenecoated Pd(0) nanoparticles on APS-functionalized SiO₂ particles were centrifugally separated from the suspension, ultrasonically washed three times with water and twice with ethanol, and dried under vacuum at 60 °C for 24 hours.

Hydrogenation reaction

Hydrogenation of 2,4-dimethyl-1,3-pentadiene and allyl alcohol was carried out in a 6 mL high-pressure stainless steel reactor with a magnetic stirrer with or without scCO₂. In the experiment, 2 mmol of substrate and the desired amount of catalyst were introduced into the reactor, and then the reactor was sealed. The air in the reactor was replaced by CO2 and the reactor was then heated to 40 °C. After the introduction of H_2 to the desired pressure, CO₂ was charged into the reactor with a highpressure pump (DB-80) to the desired pressure. The reaction was performed under stirring for a desired time. The reactor was then cooled in an ice bath and the gases were vented slowly. After the catalyst was centrifuged from the suspension, the liquid phase was analyzed by GC (Agilent 4890 D) equipped with a flame-ionized detector. The retention time of the products was compared with available authentic standards. The purity and structure of the products obtained at some typical experimental conditions were also checked by GC-MS methods. In the catalyst recycling experiments, the product and the catalyst were centrifuged at 16000 rpm for 5 min and the catalyst was reused after washing with ethanol and drying.

Characterization

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer 7 Series Thermal Analysis System. Dried samples were heated to 750 °C in air at a heating rate of 10 °C min⁻¹, and the observed mass loss was attributed to the quantitative degradation of the polystyrene. The morphologies of the samples were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which were performed on a JEOL JSM-6700F field emission microscope and on a JEOL 2010 transmission electron microscope operating at 200 kV, respectively. The Fourier transform infrared (FT-IR) spectra of the samples through compressing with KBr powder were obtained in the region of 400–4000 cm⁻¹ by using a Bruker Tensor 27 spectrometer. The contents of Pd(0) in catalyst A, B and C were 0.47%, 0.35% and 0.28%, respectively, which was determined by inductively coupled plasma optical emission spectroscopy (ICP-AES, Vista-MPX).

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