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Polymers as novel modifiers for supported metal catalyst in hydrogenation of benzaldehydes

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ABSTRACT

Polyethylene glycol (PEG) was impregnated on a palladium metal supported on silica gel and used in a catalyst for hydrogenation of benzaldehydes. In the vapor-phase flow reaction, the PEG modification improved catalytic activity and selectivity for a partially hydrogenated product, benzyl alcohol. In isoprene hydrogenation, selectivity for partially hydrogenated products, monoenes, was also enhanced. X-ray photoelectron spectroscopy (XPS) analysis of the modified catalysts revealed that the modification with PEG makes the palladium surface negatively charged, possibly leading to an increase in the selectivity for the partially hydrogenated product caused by enhancement of its desorption from the surface. In the liquid-phase hydrogenation of benzaldehyde, the PEG modification also increased the selectivity for benzyl alcohol.

1. Introduction

The development of high-performance catalysts is imperative for energy conservation and effective utilization of resources. The use of modifiers for heterogeneous catalysts is an efficient method for improving product selectivity and catalytic activity [1]. Many types of modifiers used with supported metal catalysts for hydrogenation reactions have been reported [2–4], including metal [2,3], organic [2–4], and inorganic [2,3] modifiers. These modifiers exert primarily an electronic effect on the metal surface, poison-specific active sites for the formation of by-products, and alter the morphology of the metal catalysts. The variety of modifiers allows various selective hydrogenations, and thus, the development of new modifiers is important for widening the range of possible selective hydrogenations.

In this study, we examined polymers such as polyethylene glycol (PEG) as novel modifiers for metal catalysts. Because a polymer has low vapor pressure at higher temperatures, it has an advantage as a modifier for vapor-phase reactions. Furthermore, oxygen in an ether bond can be coordinated to metal atoms on the metal surface [5,6], possibly because the metal surface is negatively charged by electrons donated from oxygen in PEG. Generally, since oxygen is weakly coordinated to the metal atoms, ordinary molecules consisting of oxygen, such as ethers, cannot remain on the surface for a long duration. However, polymers containing oxygen must remain on the metal surface or in its vicinity to continuously affect the catalytic activity. Thus, PEG is a prospective modifier to produce a negatively charged metal catalyst for various metal-catalyzed reactions. The use of PEG with metal catalysts has been previously reported [7–9]. In these reports, the metal catalyst was highly dispersed in PEG and showed high hydrogenation activity because of formation and stabilization of Pd nanoparticles in PEG. However, the role of PEGs as a modifier on metal catalysts has not been examined.

In this study, we report on the use of polymers as effective modifiers for a conventional supported palladium metal catalyst in the partial hydrogenation of benzaldehyde. Benzaldehyde is reduced to afford benzyl alcohol, which is subsequently converted to toluene and benzene. To obtain benzyl alcohol selectively, many metal catalysts such as Pd [10–12], Ni [13,14], Cu [15], and Pt [16–18] have been reported. Sulfur poisoning of palladium [10] and intercalation of palladium nanoparticles into bentonite [11] increased the selectivity for partial hydrogenation. This work demonstrates that modification with PEG improved benzyl alcohol selectivity as well as benzaldehyde conversion, and that in isoprene hydrogenation, selectivity for monoenes also increased. These results indicate that PEG modification could potentially be applied to various hydrogenations.

2. Experimental

2.1. Catalyst preparation

A silica-supported palladium metal catalyst, Pd/SiO_2, was prepared in the following manner. Silica gel Q-15 (surface area

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194 $m^2 g^{-1}$, pore volume 0.95 mL g^{-1}, from Fuji Silysia Chemical Ltd.) was dried at 200 °C for 24 h in an oven. Tetraamminepalladium(II) chloride ($Pd(NH_3)_4Cl_2 \cdot H_2O$, 98%, Aldrich) was impregnated on the dried silica using the incipient wetness method. The amount of palladium was 0.1% (w/w) of silica gel. After drying at 40 °C in vacuum (20 Torr), the catalyst was calcined at 400 °C for 12 h. Before the hydrogenation, palladium was reduced at 150 °C for 1 h in a stream of hydrogen. PEG-modified Pd/SiO_2, PEG-Pd/SiO_2 (Pd 21% (w/w)), was prepared by impregnation of PEG (0.42 g, average molecular weight: 1000, specific gravity: 1.13 g mL^{-1}, Kanto Chemical Co., Inc.) using its aqueous solution (4.5 mL) on calcined $Pd(NH_3)_4Cl_2$-impregnated silica (2 g). After drying at 40 °C in vacuum (20 Torr), the catalyst was reduced at 150 °C for 1 h in a stream of hydrogen. Long-chain PEGs (PEG(8200), average molecular weight: 8200, Kanto Chemical Co., Inc.; PEG(500,000), average molecular weight: 500,000, Kanto Chemical Co., Inc.) and polypropylene glycol (PPG, average molecular weight: 400, Wako Pure Chemical Industries) were impregnated using their aqueous solutions, whereas ethanol and toluene were used as solvents for impregnation of polydimethylsiloxane (DMPS, SH200, Dow Corning Toray Co.) and polyvinyl butyral (PVB, average molecular weight: 300, Wako Pure Chemical Industries), respectively.

2.2. Reaction procedure

Vapor-phase hydrogenation was performed in an atmospheric fixed-bed flow reactor. The catalyst, 0.05 g (excluding polymer weight), was placed in a quartz reactor (id: 10 mm). After reduction of the catalyst at 150 °C for 1 h in a stream of hydrogen (25 mL min^{-1}), benzaldehyde vapor (0.43 kPa) and hydrogen (33.3 kPa) were fed into the reactor, with nitrogen as a balance gas. The contact time, W/F [$L/(L_{liquid}\ h^{-1})$], was 3.5 h. Products were collected for 1 h and analyzed by gas chromatography and gas chromatography–mass spectrometry.

Liquid-phase hydrogenation was performed in a 50-mL autoclave. After reduction of the catalyst (0.2% (w/w) Pd/SiO_2) at 150 °C for 1 h in the quartz tube reactor in a stream of hydrogen (25 mL min^{-1}), 0.05 g (excluding polymer weight) of the catalyst was transferred into the autoclave in a nitrogen atmosphere. Benzaldehydes (2 mL) and dodecane (25 mL) as a solvent were put in the autoclave and hydrogen was charged at 3 MPa. The hydrogenation was performed at 180 or 190 °C. After the reaction, the autoclave was cooled, and butanol as an internal standard was added to the reaction mixture.

2.3. Catalyst characterization

Nitrogen adsorption was measured with a BELSORP-mini (BEL Japan). Prior to the measurement, the catalyst was dried at 120 °C for 3 h under evacuation. Pore size distributions were calculated using desorption isotherms. X-ray diffraction (XRD) patterns of the catalysts were recorded using Cu Kα with a MiniFlex (Rigaku Co.). XRD samples were not ground to avoid changes in the catalyst due to heat generated by grinding. The amount of CO adsorbed on palladium was measured by consumption of CO in several pulses (0.63 mL) of 20% CO (in helium) at room temperature, after 0.2 g of the catalyst was reduced at 150 °C for 1 h in a hydrogen stream. Transmission electron microscopy (TEM) images were taken using a JEM-2010F (JEOL) operated at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA-3200 (Shimadzu Co.). Mg Kα (1253.6 eV, 8 kV, 30 mA) was used as incident radiation. The Au 4f 7/2 binding energy of 83.8 eV was used as an internal standard to correct for electrostatic charging.

3. Results and discussion

3.1. Vapor-phase hydrogenation of benzaldehyde

3.1.1. Vapor-phase hydrogenation of benzaldehyde over Pd/SiO_2 modified with PEG

Table 1 shows the results of vapor-phase hydrogenation of benzaldehyde using the polymer-modified Pd/SiO_2. The use of an unmodified catalyst resulted in the formation of toluene as a by-product, together with benzyl alcohol. Modification with 21% (w/w) PEG increased benzyl alcohol selectivity to 100% and increased benzaldehyde conversion; PPG also improved the selectivity. At almost 100% benzaldehyde conversion, the addition of the polymer enhanced the selectivity remarkably, as shown in Table 2. The selectivity increased with an increase in the amount of polymer; however, an increase in polymer amount also decreased the conversion, possibly because a larger amount of palladium present on the surface was covered with the polymer. A catalyst prepared by impregnation with an aqueous mixture of PEG and tetraamminepalladium(II) chloride solution gave almost the same conversion and selectivity. This indicates that differences in catalyst preparation procedures do not affect the catalytic property of palladium. PEG (21% (w/w))-modified Pd/SiO_2 showed constant conversion and selectivity for 5 h on stream.

Thermogravimetric analysis of the used catalyst revealed that almost all PEG still remained on the catalyst. We have reported that PEG was used as a liquid medium in a supported liquid-phase

Table 1
Vapor-phase hydrogenation of benzaldehyde using polymer-modified Pd/SiO_2.

Catalyst	Polymer amount [% (w/w)]	Benzaldehyde conversion (%)	Selectivity (%)	
			Benzyl alcohol	Toluene
Pd/SiO_2[a]	0	59	92	8
PEG-Pd/SiO_2[a]	21	71	100	0
PEG-Pd/SiO_2[a]	66	57	100	0
PPG-Pd/SiO_2[a]	21	59	100	0
Pd/SiO_2[b]	0	25	90	0
PEG-Pd/SiO_2[b]	21	45	98	2

[a] 0.1% (w/w) Pd/SiO_2 0.05 g, W/F = 3.5 h, reaction temperature 100 °C, benzaldehyde 0.43 kPa, H_2 33.3 kPa.

[b] 1% (w/w) Pd/SiO_2 3.5 mg, W/F = 0.037 h, reaction temperature 100 °C, benzaldehyde 0.22 kPa, H_2 14.4 kPa.

Table 2
Benzaldehyde conversion and product selectivity in vapor-phase hydrogenation of benzaldehyde at almost 100% benzaldehyde conversion.

Polymer	Polymer amount [% (w/w)]	Benzaldehyde conversion (%)	Selectivity (%)	
			Benzyl alcohol	Toluene
None	0	100	49	51
PEG	2.1	99	89	11
PEG	21	98	95	5
PEG	66	91	93	7
PEG[a]	21	100	92	8
PEG(8200)	21	99	89	11
PEG(500,000)	21	12	88	12

[a] Prepared by impregnation with a mixture of PEG and $Pd(NH_3)_4Cl_2$ 0.1% (w/w) Pd/SiO_2 0.15 g, W/F = 4.9 h, reaction temperature 120 °C, benzaldehyde 0.86 kPa, H_2 67.1 kPa.

catalyst for vapor-phase reactions at higher reaction temperature than 120 °C (hydrogenation temperature in Table 2) [19–21]. In this catalyst system, PEG was not lost through vaporization during the reaction. These results strongly suggest that the PEG-modified catalyst is stable. When the PEG-modified Pd/SiO_2 was reused after the first reaction, the catalyst still showed the same conversion after three times; however, the selectivity decreased slightly from 95% to 91%, which is still higher than that of the reaction catalyzed by Pd/SiO_2. This indicates that the PEG-modified catalyst is reusable.

3.1.2. Pd/SiO_2 modified with various polymers

The effects of various polymers on the reaction were examined. Modification of PEG(8200) or PVB also improved the selectivity; however, it was still low, as shown in Tables 2 and 3. Further lengthening of the PEG chain (PEG(500,000)) decreased the conversion remarkably. The particles of Pd/SiO_2 modified with PEG(500,000) were aggregated because their external surface was adhesive. This indicates that the external surface of the catalyst was covered with PEG and that PEG hindered access of the reactant to the palladium metal surface. When 1,2-diethoxyethane (DEE), which is one unit of PEG, was fed to the reactor with benzaldehyde and hydrogen, selectivity was also observed to improve. Improvement in the selectivity by modification with PEG, PPG, or PVB, or through co-feed of DEE indicates that coordination of oxygen in an ether bond to palladium metal atoms affects the selectivity. Polydimethylsiloxane (PDMS) having oxygen in a siloxane bond decreased the conversion slightly and did not affect the selectivity. The external surface of the catalyst modified with PDMS was also adhesive. Impregnation of PDMS only on the external surface of the catalyst possibly causes no effect of PDMS modification. Thiophene was adsorbed by feeding gaseous thiophene (2.5% of palladium amount) to the reactor before the hydrogenation. Sulfur in thiophene did not influence the selectivity.

3.2. Vapor-phase hydrogenations of isoprene and crotonaldehyde

Isoprene hydrogenation was also performed using polymer-modified Pd/SiO_2. Modification with PEG increased the selectivity for pentenes to 91%. Although change in the isoprene conversion with the PEG modification was small and close to the experimental errors, the conversion increased from 30% to 35% (Table 4). Improvement in the selectivity for partial hydrogenation (probably also in the catalytic activity) was consistent with the results for benzaldehyde hydrogenation. However, in crotonaldehyde hydrogenation at 90 °C, 2.9 kPa of crotonaldehyde and 16 kPa of hydrogen, the modification with PEG decreased the conversion from 54% to 19%, and only butyraldehyde was formed, regardless of the PEG used. The modification is likely to have no effect on the selectivity for crotonalcohol formed via a different path.

3.3. Characterization of the PEG-modified catalyst

3.3.1. Pore size distribution

The effect of PEG amount on pore size distribution and pore volume was examined using nitrogen adsorption–desorption. Pore size distributions of the PEG-modified catalysts and pore volumes are shown in Fig. 1 and Table 5, respectively. Pore volume decreased with increasing PEG amount, and a decrease in pore volume was close to the volume of PEG loaded on silica, indicating that the pore openings are not plugged with PEG. Modification with 21% (w/w) PEG decreased pore size. When a higher amount (66% (w/w)) of PEG was used, pore size was the same as that using 21% (w/w) PEG and peak intensity of pore size decreased. This indicates that using 21% (w/w) PEG, pore walls are uniformly coated with PEG; however, use of 66% (w/w) PEG leads to partially filling pores with PEG. This causes lower catalytic activity of 66% (w/w) PEG-modified catalysts (Tables 1 and 2). When 21% (w/w) PEG

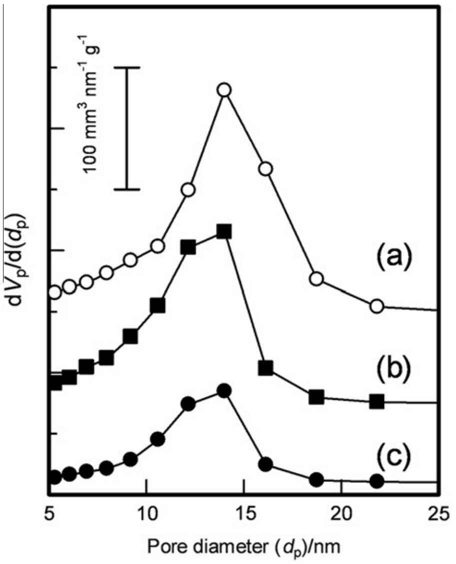


Fig. 1. Pore size distribution of PEG-modified Pd/SiO_2. PEG amount (a) 0%, (b) 21% and (c) 66% (w/w).

Table 3
Vapor-phase hydrogenation of benzaldehyde using Pd/SiO_2 catalyst with various modifiers.

Modifier	Modifier	Benzaldehyde	Selectivity [%]		
	Amount [% (w/w)]	Conversion (%)	Benzyl alcohol	Toluene	Benzene
None	–	29	91	8	1
PEG	24	35	96	3	1
PVB	3	25	94	5	1
PDMS	3	27	92	7	1
DEE	6 kPa[a]	32	94	5	1
Thiophene	2.5%[b]	26	91	8	1

0.1% (w/w) Pd/SiO_2 0.06 g, W/F = 1.3 h, reaction temperature 120 °C, benzaldehyde 2.0 kPa, H_2 32 kPa.

[a] 1,2-Diethoxyethane was fed with benzaldehyde and hydrogen.

[b] Thiophene was adsorbed before the hydrogenation. The amount of adsorbed thiophene was 2.5% of the surface palladium atoms.

Table 4
Vapor-phase hydrogenation of isoprene using PEG-modified Pd/SiO_2.

Catalyst	Isoprene conversion (%)	Selectivity (%)			
		2-Methyl-1-butene	2-Methyl-2-butene	3-Methyl-1-butene	Isopentane
Pd/SiO_2	30	12	57	4	27
PEG-Pd/SiO_2	35	19	65	7	9

0.1% (w/w) Pd/SiO_2 0.016 g, PEG 0.21% (w/w). W/F = 0.030 h, reaction temperature 70 °C, time on stream 5 h, isoprene 13 kPa, H_2 49 kPa.

Table 5
Pore volume of PEG-modified Pd/SiO_2.

PEG amount [% (w/w)]	PEG volume (mL g^{-1})	Pore volume[a] (mL g^{-1})
0	0	1.15
21	0.19	1.01
66	0.58	0.65

[a] Excluding polymer weight.

was used for preparation of the catalyst, which was the most effective among the prepared catalysts, the thickness of the PEG layer was calculated to be ca. 1 nm.

3.3.2. Palladium particle size

To clarify the effect of PEG modification, palladium particle size was examined. Transmission electron microscope (TEM) analysis revealed that palladium particles are spherical and that palladium particle sizes of the unmodified and modified Pd/SiO_2 were the same, i.e. 5 nm (Fig. 2a and b). It is known that in PEG medium metal nanoparticles are formed and stabilized [7–9]. However, on the silica support, PEG did not affect the particle size. This indicates that enhancement in the conversion and the selectivity by PEG modification is not due to a change in the size of the palladium particles. Thus, PEG modification affects properties of surface palladium atoms.

3.3.3. Adsorption of carbon monoxide

To estimate the amount of palladium atoms on the surface, the amount of carbon monoxide (CO) adsorbed at room temperature was measured. Assuming that one molecule of CO is adsorbed on one palladium metal atom, the amount of surface palladium atoms in the unmodified catalyst was 1.6×10^{-6} mol $g_{cat}{}^{-1}$. On the other hand, the catalyst modified with 21%(w/w) PEG had 7.1×10^{-7} mol $g_{cat}{}^{-1}$ of surface palladium atoms. Thus, CO adsorption results and the fact that there was no change in particle size (TEM results) show that 56% of the surface atoms were covered with PEG. In the measurement of CO adsorption at room temperature, PEG was solid. However, under reaction conditions, PEG became liquid. It is possible that the reactants dissolved in the liquid PEG and were exposed to the palladium surface through PEG overlayers. Supposing that there are no reactants passing through the PEG layers, the turnover frequency of the surface atoms increased remarkably (from 2.9×10^3 h^{-1} to 7.5×10^3 h^{-1}, as shown in Table 1) when modified with PEG.

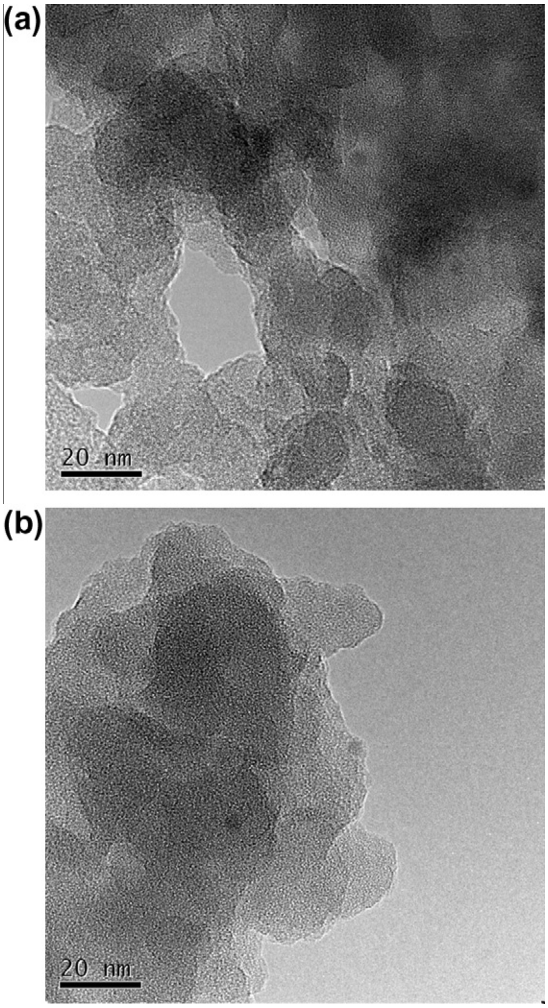


Fig. 2. TEM images of: (a) Pd/SiO_2 and (b) PEG-modified Pd/SiO_2. Pd amount was 0.1% (w/w).

3.3.4. X-ray photoelectron spectroscopy

Coordination of oxygen in the polymer to the palladium metal atoms was expected to improve the catalytic activity. The electronic state of the palladium surface was examined by X-ray photoelectron spectroscopy (XPS). Fig. 3 shows the Pd 3d spectra of the unmodified and modified catalysts. Since the amount of palladium in the catalyst used for the reaction was very low (0.1% (w/w), it was below the detection limit of XPS. Therefore, the catalyst of 1% (w/w) of palladium was used for XPS analysis. When 1% (w/w) palladium catalysts were used for the hydrogenation of benzaldehyde, the modification with PEG enhanced the product yield and the selectivity for benzyl alcohol (Table 1). In the unmodified catalyst, peaks at 335.0 and 340.4 eV assigned to palladium metal were observed (Fig. 3). Modification with PEG decreased the binding energy of Pd 3d peaks. This indicates a decrease in electron density of Pd. In the spectrum of the PEG-modified catalyst, one Pd $3d_{5/2}$ peak was observed and its peak intensity was low, indicating that all Pd particles were partially covered with PEG. Therefore, the hypothesis that some Pd particles were coated and some were not is incorrect.

3.3.5. Schematic of PEG-modified catalyst

TEM observation and nitrogen adsorption showed that palladium particles are spheres with ca. 5 nm diameters and that the pore wall is uniformly coated with 1-nm layers of PEG, respectively. Fig. 4 shows our proposed schematic of PEG-modified catalyst. As mentioned above, CO adsorption results show that 56% of the surface atoms were covered with PEG. We speculated that the bottom of the palladium particles is buried in PEG layers and the top is partially coated with thin PEG layers. Benzaldehyde possibly accesses the palladium surface through openings of the PEG layers on the palladium particles.

Generally, the effects of modifiers on catalytic properties of metal catalysts are changes in size and morphology of metal particles,

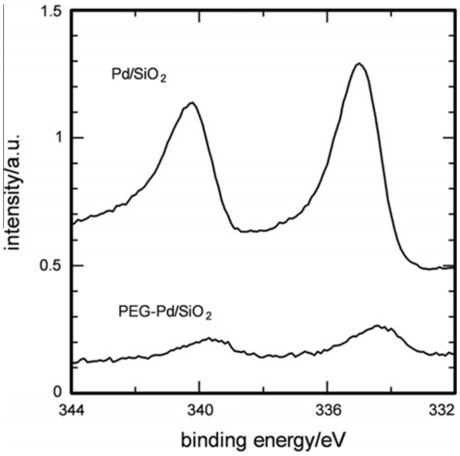


Fig. 3. X-ray photoelectron spectra of the Pd 3d region of Pd/SiO_2 and PEG-modified Pd/SiO_2 after reduction at 150 °C for 1 h in a stream of hydrogen. Pd and PEG amounts were 1% and 21% (w/w), respectively.

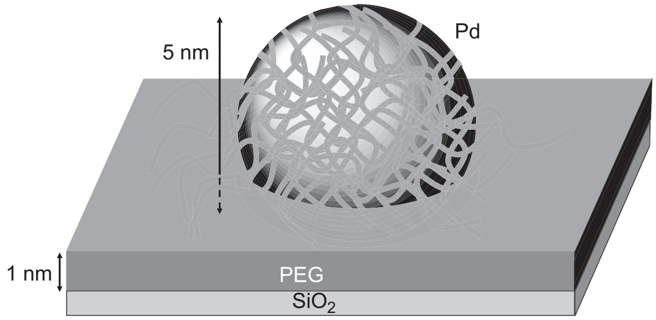


Fig. 4. Proposed schematic of PEG-modified Pd/SiO_2.

steric effects on reaction intermediates, and changes in electronic state of metal surface. When PEG was used as the modifier, the modification did not affect particle size and morphology of palladium particles. PEG weakly interacts with palladium atoms on the surface because coordination strength between oxygen and the metal is much weaker than sulfur and nitrogen. Thus, at the reaction temperature, it is possible that PEG can move on the surface, leading to no steric effect.

To prepare PEG-modified Pd/SiO_2, PEG was impregnated on the reduced Pd/SiO_2. It is possible that palladium atoms on the surface are partially oxidized during PEG impregnation, and Chen and Chen reported that adsorbed oxygen on Pd/SiO_2 enhanced the formation of ethylbenzene in acetophenone hydrogenation [22]. We tried to partially oxidize Pd/SiO_2 in a 4% O_2(4%)–He mixture stream at 100 °C for 30 min. Pre-oxidation did not improve the conversion nor the selectivity in vapor-phase hydrogenation of benzaldehyde because the oxidation temperature was lower than that in the report [22] and reduction of the catalyst was carried out prior to the hydrogenation. This indicates that partial oxidation of palladium metal during PEG impregnation does not cause the improvement.

XPS analysis of the catalysts revealed that modification with PEG makes the palladium surface negatively charged, and we concluded that this is the most important effect of PEG modification on catalytic properties. It was reported that the Langmuir–Hinshelwood mechanism is applicable to benzaldehyde hydrogenation and that low surface coverage of benzyl alcohol brings about high selectivity for benzyl alcohol [17]. We speculated that repulsion between the oxygen of benzyl alcohol and the negatively charged palladium surface promotes benzyl alcohol desorption from the surface, leading to the inhibition of further hydrogenation. Thiophene can also be coordinated to the metal surface; however, thiophene is an electron acceptor [23]. As shown in Table 3, pre-adsorption of thiophene on the catalyst did not improve the selectivity.

Piperidine was reported as an electron-donating modifier for palladium catalysts in hydrogenations of 1-butene and 1,3-butadiene, and the modification resulted in a remarkable decrease in a turnover number for 1-butene hydrogenation and a slight change in that for 1,3-butadiene [24], indicating that electron-rich palladium catalysts show high selectivity for monoenes in diene hydrogenation. This is consistent with the result that PEG modification increased selectivity for the monoenes in isoprene hydrogenation (Table 4).

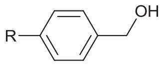
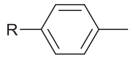
In isoprene hydrogenation, 2-methyl-2-butene is formed by 1,4-addition of hydrogen to isoprene and also by simultaneous isomerization of 2-methyl-1-butene and 3-methyl-1-butene. Aduriz et al. reported that 2-methyl-2-butene selectivity increased with increasing conversion of isoprene due to the isomerization of 2-methyl-1-butene and 3-methyl-1-butene [25]. Modification with PEG slightly decreased the product distribution of 2-methyl-2-butene among pentenes (Table 4) even at a higher isoprene conversion. It is plausible that repulsion between negatively charged palladium and methyl-1-butenes enhances their desorption from the catalyst before the isomerization.

3.4. Liquid-phase hydrogenation of benzaldehydes

To examine the effect of PEG modification on hydrogenations of various benzaldehydes, the reactions of *p*-anisaldehyde and *p*-tolualdehyde were carried out in a liquid phase, because their vapor pressures were too low to feed them by vapor to the reactor at a reaction temperature. Dodecane was used as a solvent because the solubility of PEG in it is very low. The results are summarized in Table 6. To compare the selectivities for partial hydrogenation at the same conversion, the catalyst amount and reaction time were adjusted. Improvement in the selectivity for the partial hydrogenation was observed, indicating that PEG modification can be applied to hydrogenations of various benzaldehydes. However, the catalytic activity decreased, which is contrary to the results in the vapor-phase flow reaction.

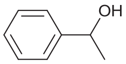
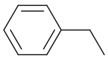
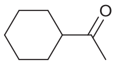
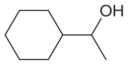
It is plausible that in the vapor-phase reaction, PEG holds benzaldehyde to increase its residence time in the catalyst bed in the flow reactor, causing an increase in the conversion. On the other hand, in the liquid-phase reaction, it is likely that charging palladium negatively by PEG modification also causes improvement in the selectivities. Decreasing the benzaldehyde conversion is probably caused by decreasing the number of surface palladium atoms by PEG modification and the fact that an increase in the residence times of the reactants in the flow system is not observed in the batch system.

Table 6
Liquid-phase hydrogenation of benzaldehydes using PEG-modified Pd/SiO_2.

Polymer	Catalyst amount (mg)	Reaction time (h)	Benzaldehydes conversion (%)	Selectivity (%)	
					
Benzaldehyde (R: H)[a]					
None	50	2	84	98	2
PEG	80	2	84	100	0
p-tolualdehyde (R:CH_3)[b]					
None	50	5	18	75	25
PEG	90	5	23	95	5
p-anisaldehyde (R:CH_3O)[b]					
None	50	1.5	35	98	2
PEG	300	6	32	100	0

[a] Palladium 0.2% (w/w), reaction temperature 180 °C, benzaldehydes 2 mL, H_2 3 MPa, dodecane 25 mL.
[b] Palladium 0.2% (w/w), reaction temperature 190 °C, benzaldehydes 2 mL, H_2 3 MPa, dodecane 25 mL.

Table 7
Liquid-phase hydrogenation of acetophenone using PEG-modified Pd/SiO_2 and PEG-modified Pt/SiO_2.

Polymer	Catalyst amount (mg)	Reaction time (h)	Acetophenone conversion (%)	Selectivity (%)			
							
Pd/SiO_2							
None	50	3	64	97	3	0	0
PEG	80	3	72	99	1	0	0
Pt/SiO_2							
None	50	1	14	59	0	38	3
PEG	50	15	13	90	0	10	0

Palladium 0.2% (w/w), reaction temperature 180 °C, acetophenone 2 mL, H_2 3 MPa, dodecane 25 mL.

When the catalyst was recycled four times in the liquid-phase hydrogenation of benzaldehyde, neither the conversion nor the selectivity decreased, indicating that the catalyst is reusable in the liquid phase.

3.5. Liquid-phase hydrogenation of acetophenone catalyzed by PEG-modified Pt/SiO_2

Modification of a supported platinum catalyst with PEG also affected the product selectivity. When the palladium catalyst was used for liquid-phase hydrogenation of acetophenone, products were 1-phenylethanol and ethylbenzene. PEG modification slightly increased the selectivity for 1-phenylethanol (Table 7). On the other hand, when the platinum catalyst was used, a benzene ring of acetophenone was also hydrogenated; i.e. products were 1-phenylethanol, 1-phenylethanone and 1-cyclohexylethanol. PEG modification of the platinum catalyst inhibited the hydrogenation of the benzene ring. Repulsion between the benzene ring of acetophenone and the negatively charged palladium surface possibly inhibits the hydrogenation of the benzene ring.

4. Conclusions

Polyethylene glycol (PEG) was impregnated on a silica-supported palladium metal catalyst for benzaldehyde hydrogenation. In a vapor-phase flow hydrogenation, PEG modification increased the selectivity for benzyl alcohol and the benzaldehyde conversion. On the other hand, in a liquid-phase hydrogenation, the modification increased the selectivity but decreased the conversion. XPS analysis of the catalysts revealed that palladium atoms on the surface are charged negatively after PEG modification. Instead of PEG, use of polypropylene glycol and polyvinyl butyral or co-feed of 1,2-diethoxyethane to the reactor also increased the selectivity. These results indicate that oxygen of PEG is coordinated to palladium atoms on the surface, and possibly repulsion between benzyl alcohol and the electron-rich palladium on the surface leads to inhibiting further hydrogenation to form toluene. In the vapor-phase flow reaction, it is plausible that increasing residence time of the reactant on the catalyst layer causes increasing the conversion. In the hydrogenations of various benzaldehydes and isoprene, the addition of PEG to the catalyst enhanced the selectivity for partially hydrogenated products. Furthermore, PEG modification also affected the catalytic properties of a supported platinum catalyst for acetophenone hydrogenation. In conclusion, modification with polymers, particularly PEG, has the potential to be applied to various hydrogenations in a liquid phase as well as in a vapor phase. It is notable that PEG is suitable for the modifier because PEG is inexpensive, non-toxic, readily available, and stable.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.10.008.

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