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Palladium Supported on an Acidic Resin: A Unique Bifunctional Catalyst for the Continuous Catalytic Hydrogenation of Organic Compounds in Supercritical Carbon Dioxide

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Abstract: 1% Palladium-doped acidic resin (Amberlyst® 15; styrene-divinylbenzene matrix with sulfonic acid groups) is shown to be a highly active catalyst for the continuous catalytic hydrogenation of C=C bonds in supercritical carbon dioxide ($scCO_2$) without affecting C=O bonds. This 1% Pd/Amberlyst-15 catalyst promotes the industrially important selective formation of 2-ethylhexanal from crotonaldehyde in a "one-pot" pathway involving hydrogenation and aldol condensation with a number of merits. The selectivity behavior of 1% Pd/Amberlyst-15 is strikingly different compared to that of 1% Pd/C and 1% Pd/Al_2O_3 due to its prominent bifunctional nature based on sulfonic acid groups adjacent to metallic Pd sites. Hybrid "$[Pd_n\text{–}H]^+$" sites are suggested to act as both metal and acid sites promoting the bifunctional catalysis.

Keywords: Amberlyst® 15-supported palladium catalyst; bifunctional catalysis; continuous-flow reactor; hydrogenation; one-pot reaction; supercritical carbon dioxide

Introduction

Supercritical carbon dioxide ($scCO_2$) is an attractive reaction medium due to its non-toxicity, non-flammability, and low cost. Its great miscibility with gases as well as liquid organic compounds enhances the gas-liquid mass transport, and thus can accelerate those reactions whose rates are determined by gas-liquid mass transfer. These features, together with the low viscosity and high diffusivity, render $scCO_2$ suitable particularly for heterogeneous catalytic hydrogenations and oxidations.[1–3] Most catalysts used so far under such conditions were conventional ones, while corresponding studies based on specifically developed new catalysts are still scarce.

Amberlyst® 15 is a commercially available, strongly acidic cation exchange resin composed of styrene-divinylbenzene matrix with sulfonic acid groups and has been used as a heterogeneous acid catalyst with great success.[4] Laufer and Hoelderich first introduced transition metal loaded on Amberlyst® 15 as catalyst and reported that the support acidity assisted the catalysis by surface palladium and platinum for the hydroxylation of benzene.[5] The transition metal/Amberlyst® 15 catalysts seem to have a great potential for environmentally friendly chemical productions, where both a transition metal and acidic conditions are required, because the use of hazardous homogeneous acids such as hydrochloric acid and sulfuric acid can be avoided. In addition, these catalysts may provide the opportunity to achieve "one-pot" synthesis through the transition metal-acid bifunctional catalysis pathways.

Quite recently, Hoelderich's group reported an efficient one-pot synthesis of a potential analgesic over Amberlyst® 15-supported palladium catalyst in ethanol solvent, which involves dehydration and subsequent hydrogenation.[6] A number of acidic supports including inorganic oxides were tested, but only Amberlyst® 15 promoted the dehydration process smoothly, showing that Amberlyst® 15 is an excellent support for this kind of dehydration-hydrogenation one-pot reaction. However, the three-phase reaction system with the inherent gas-liquid-solid mass transport problem required a high reaction temperature of 150 °C, which caused unfavorable coke formation and the deterioration of the surface sulfonic acid groups. Actually, the original activity of the catalyst could not be restored in the second reaction cycle even after careful washing of the used catalyst.

We have concurrently communicated that palladium-doped Amberlyst® 15 directly affords 2-ethylhexanal from crotonaldehyde in $scCO_2$ *via* hydrogenation and aldol condensation.[7] Owing to the great miscibility of the substrate and gaseous hydrogen in $scCO_2$, the reaction could be performed at a low temperature of 60°C and with a slight excess amount of H_2. A good long-term catalytic behavior was observed under the optimal conditions, in which almost 100% conversion was maintained for at least 12 h and the only by-product was butyraldehyde. The use of $scCO_2$ medium is thus one of the promising ways to improve the efficiency of the catalyst for one-pot reactions involving hydrogenation.

Here we report a systematic study of the unique bifunctional catalysis of palladium-doped Amberlyst® 15 in the continuous catalytic hydrogenation in $scCO_2$ and provide insight into the structural properties of the catalyst using X-ray absorption near edge structure (XANES), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and CO chemisorption combined with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

Results and Discussion

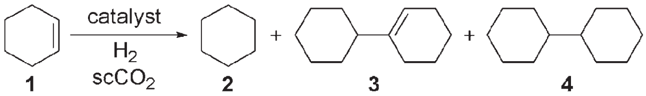
Reaction of Cyclohexene

The hydrogenation of cyclohexene **1** to cyclohexane **2** was selected as a test reaction for screening the efficiency of various supported transition-metal catalysts for the C=C bond hydrogenations in $scCO_2$. The results of these screening tests are shown in Table 1. Commercially available 1% Pd/Al_2O_3 exhibited a low activity under the reaction conditions (entry 1), while 1% Pd/C showed excellent catalytic activity (entry 2). The selectivities to **2** exceeded 99% for the commercial catalysts. The present results with 1% Pd/C are in accordance with the former data published by Arunajatesan et al.[2e]

Palladium immobilized on an acidic resin of Amberlyst® 15 (Pd/Amberlyst-15) also exhibited high activity (entries 3–5). The activity strongly depended on the amount of palladium loaded, and the catalyst containing 1% palladium showed the highest activity (entry 4). Repeating synthesis of 1% Pd/Amberlyst-15 showed that the conversion and selectivity of the catalyst were in the range 95–99 and 97 to >99%, respectively, which are comparable to or even higher than those obtained with a representative hydrogenation catalyst of 1% Pd/C. In contrast to Pd/Amberlyst-15, corresponding platinum, ruthenium, and rhodium catalysts were far less active (entries 6, 8, and 9). Addition of 0.5% Pt to 0.5% Pd/Amberlyst-15 caused a negative effect (entry 3 *vs.* 7). The by-products formed over the metal-loaded Amberlyst® 15 were the dimerization product **3**, which was formed by the action of Brönsted acid sites on Amberlyst® 15,[8] and its hydrogenated product, bicyclohexyl **4**.

Note that the 1% Pd/Amberlyst-15 catalyst showed a long lifetime for the hydrogenation, maintaining its high activity and selectivity for at least 12 h from the first sampling. This indicates that this catalyst is free from deactivation caused by unfavorable side reactions such as the reverse water gas shift reaction[9] and the oligomerization of **1**[2e]. Moreover, the long lifetime implies that the active palladium species on 1% Pd/Amberlyst-15 are tightly immobilized on the

Table 1. Reaction of cyclohexene **1** with H_2 over the supported transition-metal catalysts in $scCO_2$.[a]



Entry	Catalyst		Conversion[b] [%]	Selectivity[b] [%] 2	3	4
1	1%	Pd/Al_2O_3	26	>99	<1	<1
2	1%	Pd/C	96	>99	<1	<1
3	0.5%	Pd/Amberlyst-15	86	95	1	3
4	1%	Pd/Amberlyst-15	99	>99	<1	<1
5	2%	Pd/Amberlyst-15	56	99	<1	<1
6	1%	Pt/Amberlyst-15	2	52	46	2
7	0.5%,0.5%	Pd,Pt/Amberlyst-15	59	96	2	2
8	1%	Ru/Amberlyst-15	4	94	6	<1
9	1%	Rh/Amberlyst-15	1	24	75	1

[a] *Reaction conditions:* catalyst, 1.00 g; total pressure, 16 MPa; reactor temperature, 60°C; flow rate of expanded gaseous CO_2, 1 $L\,min^{-1}$; flow rate of **1**, 0.5 $mL\,min^{-1}$; **1**:H_2 = 1:1.8.

[b] Determined by GC.

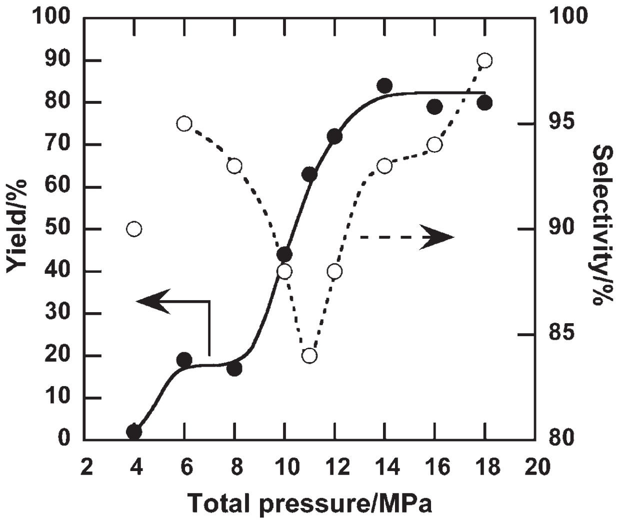


Figure 1. Dependence of the yield (●) and selectivity (○) on the total pressure. *Reaction conditions:* catalyst, 0.50 g of 1% Pd/Amberlyst-15; reactor temperature, 60 °C; flow rate of expanded gaseous CO_2, 1 L min^{-1}; flow rate of **1**, 0.5 mL min^{-1}; **1**:H_2 = 1:1.8.

catalyst surface in a stable form and that no significant metal leaching occurred upon exposure to the reaction conditions. Palladium in this type of catalyst is also stable and does not show any leaching even in polar ethanol solvent and at a higher temperature of 150 °C, as recently demonstrated by Wissler et al.[6]

Figure 1 shows the variation of the yield and selectivity as a function of the total pressure at 60 °C. The total pressure was varied by changing the CO_2 amount in the reactor, while feed rates of CO_2, **1**, and hydrogen were constant throughout the experiments. At 4 MPa, the reaction hardly proceeded, giving **2** in a low yield of 2%. Increasing the pressure from 4 to 8 MPa led to a slight increase in the yield. Further increase in the pressure up to 14 MPa resulted in a remarkable increase in the yield due to a drastic increase in the miscibility of hydrogen and **1** in $scCO_2$, which was caused by the noticeable increase in CO_2 density. Above 14 MPa, the yields were almost constant. Visual observation of the phase behavior conducted in a specially designed view-cell under similar conditions revealed that in the total pressure region of 10–14 MPa the mixture of **1**, H_2, and CO_2 transforms from a CO_2-expanded liquid-gas (two-phase system) to a single homogeneous phase; this transition is accompanied by a drastic increase of the reaction rate (Figure 1). Thus elimination of the gas-liquid interface is crucial to achieve the highest performance of 1% Pd/Amberlyst-15 as C=C bond hydrogenation catalyst.

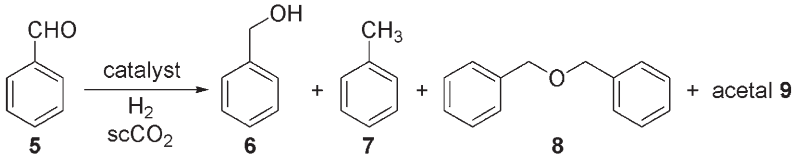
Interestingly, relatively large amounts of **3** and **4** were formed in the pressure range 10–12 MPa, which led to the decrease in selectivity. It seems that the dimerization of **1** to **3** has a large negative ΔV^{+} value in this pressure region because of the large isothermal compressibility, leading to a remarkable acceleration of the reaction with a small increase in pressure.[10] Although the observed yields of **3** and **4** were still low, this phenomenon may open up a new strategy for "one-pot" production of bicyclohexyl from cyclohexene.

Reaction of Benzaldehyde

Palladium catalysts are usually effective for the hydrogenation of ArCHO to $ArCH_2OH$ (Ar = aryl), whereas they are inefficient in catalyzing the hydrogenation of aliphatic aldehydes.[11] Nevertheless, to our knowledge, only Poliakoff's group reported the heterogeneous Pd-catalyzed hydrogenation of benzaldehyde **5** in $scCO_2$.[2b] With a 5% Pd/aminopolysiloxane catalyst, they performed the reaction at 95 °C and a total pressure of 12 MPa, employing a **5**:H_2 molar ratio of 1:2.0. Under the conditions applied, **5** was completely converted into benzyl alcohol **6** and toluene **7** with selectivities of 92 and 8%, respectively.

The 1% Pd/Amberlyst-15 and the commercial Pd catalysts were next applied for the hydrogenation of **5**, although the conditions were different from those employed by Poliakoff et al. The results are shown in Table 2. Highly selective formation of **6** was observed with the 1% Pd/Al_2O_3 catalyst, but the conversion was unsatisfactory from a synthetic point of view (entry 1). Due to the low activity observed also for the hydrogenation of cyclohexene (this study), 1% Pd/Al_2O_3 is not suitable for multiple bond hydrogenations under the conditions applied. Both the 1% Pd/C and 1% Pd/Amberlyst-15 yielded toluene **7**, dibenzyl ether **8**, and an unidentified product **9**[12] in addition to **6** (entries 2 and 3). The detailed mechanisms of the by-product formations are still unknown. However, even if part of **6** was consumed for the production of by-products, it can be stated that the activity for the hydrogenation of **5** to **6** was much lower for 1% Pd/Amberlyst-15 than for 1% Pd/C, because the respective yields of **6** and the by-products were higher for 1% Pd/C than for 1% Pd/Amberlyst-15. Note the striking fact that the activity of 1% Pd/Amberlyst-15 for the hydrogenation of the C=C bond was almost equal to or even higher than that of 1% Pd/C (Table 1), whereas the two catalysts differed significantly in their activity for the reduction of the C=O bond, indicating the high selectivity of 1% Pd/Amberlyst-15 for C=C bond hydrogenations under the conditions applied. The low activity of 1% Pd/Amberlyst-15 for the hydrogenation of the C=O bond may be due to the following reasons: (i) the strong interaction between sulfonic acid groups and carbonyl oxygen of benzaldehyde inhibits the adsorption of the C=O

Table 2. Reaction of benzaldehyde **5** with H_2 over the supported Pd catalysts in $scCO_2$.[a]



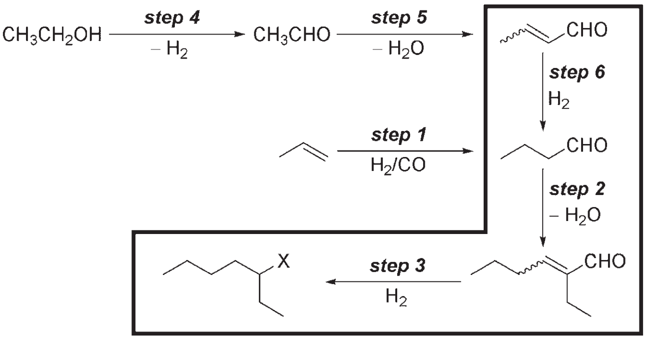
Entry	Catalyst		Conversion[b] [%]	Selectivity[b] [%]			
				6	**7**	**8**	**9**[c]
1	1%	Pd/Al_2O_3	18	100	0	0	0
2	1%	Pd/C	54	61	2	23	14
3	1%	Pd/Amberlyst-15	16	33	3	55	10

[a] *Reaction conditions:* catalyst, 1.00 g; total pressure, 16MPa; reactor temperature, 60 °C; flow rate of expanded gaseous CO_2, 1 $L\,min^{-1}$; flow rate of **5**, 0.3 $mL\,min^{-1}$; **1**:H_2 = 1:2.0.

[b] Determined by GC.

[c] Unidentified product.[12]

bond onto palladium particles; (ii) the benzaldehyde molecules strongly adsorbed on acid sites cause steric hindrance for the adsorption of other free benzaldehyde molecules onto palladium particles; the palladium particles on neutral 1% Pd/C, on the other hand, are probably easily accessible for polar benzaldehyde molecules; (iii) the surface Pd atoms on 1% Pd/Amberlyst-15 are more cationic compared to those on 1% Pd/C and presumably interact only with the oxygen atom in the C=O bond, leading to an unfavorable adsorbed conformation for the hydrogenation (see "Structural Properties of 1% Pd/Amberlyst-15" section); and (iv) the difference in the number of active Pd sites for the C=O bond hydrogenation might also be related to the different activity of 1% Pd/Amberlyst-15 and 1% Pd/C (see "Structural Properties of 1% Pd/Amberlyst-15" section).



Scheme 1. Industrial manufacturing routes to 2-ethylhexanal (**11**, X = CHO) and 2-ethylhexanol (X = CH_2OH). Reaction types: step 1, hydroformylation; step 2, aldol condensation; step 3, hydrogenation; step 4, dehydrogenation; step 5, aldol condensation; step 6, hydrogenation.

Highly Efficient Continuous "One-Pot" Production of 2-Ethylhexanal from Crotonaldehyde

The key catalytic properties of 1% Pd/Amberlyst-15 observed in the above two test reactions are: (i) high activity for C=C bond hydrogenations; (ii) low activity for C=O bond hydrogenations; and (iii) palladium-acid bifunctionality. This prompted us to apply the 1% Pd/Amberlyst-15-$scCO_2$ catalytic system for the "one-pot" synthesis that involves selective C=C bond hydrogenations and acid-catalyzed reactions. One such reaction that has great significance in chemical industry is the one-pot production of 2-ethylhexanal from C_4 aldehydes, which involves aldol condensation and hydrogenation(s). In Scheme 1 are shown the industrial synthetic routes to 2-ethylhexanal and 2-ethylhexanol. Typically these C_8 compounds are manufactured by several steps including the hydroformylation of propylene (step 1), base-catalyzed aldol condensation of butyraldehyde (step 2), and subsequent gas-phase hydrogenation of 2-ethylhexenal (step 3).[13] The major problem of the conventional multi-step process is that high capital cost plants are required for product purification, recovery, and waste treatment particularly in the aldol condensation step where homogeneous strong base catalysts must be handled safely.[14] Another drawback is the high reaction temperature required for the gas-phase hydrogenation. Thus several research groups focused on efficient bifunctional catalytic systems that convert propylene or butyraldehyde to the C_8 chemicals in one-pot pathways. Shell (USA and UK) and Exxon (USA and Japan) developed the "Aldox" process that affords 2-ethylhexanol directly from propylene by using co-catalysts such as compounds of Zn, Sn, Ti, Al or Cu or KOH in addition to the original "oxo" catalyst.[13] However, these processes have several inherent disadvantages: (i) a large excess of CO is required; (ii) the liquid space velocity in the hydroformylation is relatively low; and (iii) the selectivity to 2-ethylhexanol is rather low.[15b] Recently, Kelly and co-

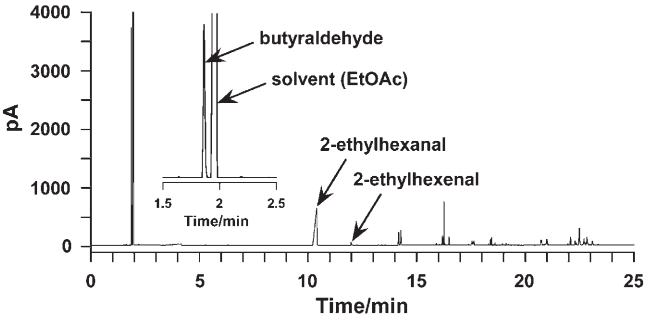


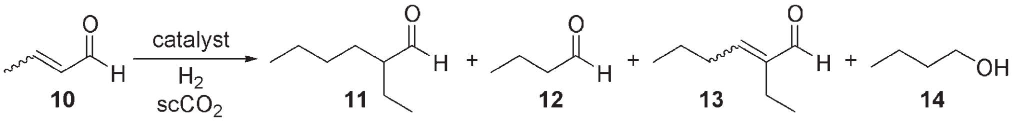
Figure 2. GC profile of the product sample obtained from the reaction of butyraldehyde **12** under the following conditions: catalyst, 1.00 g of 1% Pd/Amberlyst-15; total pressure, 16 MPa; reactor temperature, 60 °C; flow rate of gaseous CO_2, 1 L min^{-1}; flow rate of **12**, 0.3 mL min^{-1}; **12**:H_2 = 1:2.0. Column temperature conditions: 50 °C (10 min) → 20 °C min^{-1} → 250 °C (5 min). In the inset is shown a magnified view in the retention time range 1.5–2.5 min.

workers reported continuous one-step synthesis of 2-ethylhexanal from butyraldehyde using $Pd/Na/SiO_2$ as solid base hydrogenation catalyst,[15] while Sharma et al. developed $HRhCO(PPh_3)_3$ supported on hydrotalcite as a novel Aldox catalyst.[16] However, these catalytic systems require relatively high reaction temperatures (350 °C in the former and 200–250 °C in the latter) due to the low reaction rates and the yields of the C_8 products are moderate to low. In addition, several by-products are formed in both systems, which renders the product purification troublesome. Moreover, the $Pd/Na/SiO_2$ catalyst is easily deactivated by the adsorption of the C_8 product, 2-ethylhexanal.

We first attempted the one-step synthesis of 2-ethylhexanal **11** from butyraldehyde **12** with the 1% Pd/Amberlyst-15-$scCO_2$ catalytic system. However, GC analysis of the product samples indicated the formation of many unidentified products in non-negligible amounts, particularly in the later retention time region (Figure 2), as well as **11**.

We next applied the 1% Pd/Amberlyst-15-$scCO_2$ catalytic system to crotonaldehyde **10** and found that this α,β-unsaturated aldehyde is converted to **11** with high selectivity. Table 3 gives the reaction results with different catalysts and under different conditions. The 1% Pd/C catalyst with inert carbon support did not afford **11** but yielded **12**, **14**, and many unidentified products such as dimers and trimers of **10** and their derivatives (entry 2), whereas some formation of **11** was observed over 1% Pd/Al_2O_3 (entry 1). Since alumina support possesses basic sites (O^{2-} and OH^-) as well as acidic sites (Al^{3+}) and promotes aldol condensation and related reactions,[17] it was expected that the 1% Pd/Al_2O_3 catalyst functioned as palladium-base bifunctional catalyst to give **11** directly from **10** *via* hydrogenation and aldol condensation. However, the yield of **11** obtained with 1% Pd/Al_2O_3 was too low from a practical point of view. In contrast, the use of 1% Pd/Amberlyst-15 catalyst afforded **11** in much higher yields (entries 3–5). Although not only **12** but also 2-ethylhexenal **13** was contained in the product samples at a lower feed amount of H_2 (entries 3 and 4), the content of **13** was almost negligible (~0% selectivity) at a **10**:H_2 molar ratio of 1:4.0 (entry 5). Then the main by-product was only **12**, which is also industrially important and can be easily separated from **11** by distillation owing to the large difference in their boiling points (**11**, bp 162 °C; **12**, bp 75 °C). Note also that the undesirable C=O bond hydrogenations were strikingly suppressed in the 1% Pd/Amberlyst-15 catalytic system, giving 1-butanol **14** in 1% selectivity and no 2-ethylhexanol regardless of the feed rate of H_2 (**10**:H_2 ratio = 1:2.0–4.0), while 1% Pd/Al_2O_3 and 1% Pd/C afforded **14** in a higher selectivity

Table 3. Reaction of crotonaldehyde **10** with H_2 over the supported Pd catalysts in $scCO_2$.[a]



Entry	Catalyst		**10**:H_2	Conversion[b] [%]	Selectivity[b] [%]			
					11	**12**	**13**	**14**
1	1%	Pd/Al_2O_3	1:2.0	93	8	70	<1	9
2	1%	Pd/C	1:2.0	94	1	55	<1	9
3	1%	Pd/Amberlyst-15	1:2.0	89	47	46	7	1
4	1%	Pd/Amberlyst-15	1:3.0	94	59	36	4	1
5	1%	Pd/Amberlyst-15	1:4.0	98	67	32	<1	1
6[c]	1%	Pd/Amberlyst-15	1:4.0	13	<1	39	24	<1

[a] *Reaction conditions:* catalyst, 1.00 g; total pressure, 16 MPa; reactor temperature, 60 °C; flow rate of expanded gaseous CO_2, 1 L min^{-1}; flow rate of **10**, 0.3 mL min^{-1}.

[b] Determined by GC.

[c] Total pressure, 4 MPa.

of 9% even at the lowest feed rate of H_2 (**10**:H_2 = 1:2.0). The high activity of the active Pd sites on 1% Pd/Amberlyst-15 for the C=C bond hydrogenations and the low activity of them for the C=O bond hydrogenations are in good agreement with the results observed in cyclohexene and benzaldehyde hydrogenations (see the sections: "Reaction of Cyclohexene" and "Reaction of Benzaldehyde"). The GC profile of a product sample obtained under the conditions of entry 5 in Table 3 is shown in Figure 3, indicating how selective the conversion of **10** to **11** and **12** was.

The good long-term catalytic behavior of 1% Pd/Amberlyst-15 for the reaction was already shown in our preliminary communication.[7a] Here we provide selected data on the variation of the yield and selectivity with time-on-stream (Table 4). The catalyst kept yielding **11** and **12** exclusively with almost 100% conversion for at least 12 h. The selectivities to **11** and **12** did not change significantly, but the selectivity to **11** gradually decreased after 7 h accompanied by an increase in the selectivity to **12**. These results indicate that the Pd remained active on the surface during the long-term operation, whereas the number of active sulfonic acid groups gradually decreased during the reaction by deterioration or decomposition. High stability of palladium on Amberlyst® 15 has been observed also in other reactions such as the continuous hydrogenation of cyclohexene in $scCO_2$ (this study) and the one-pot synthesis of an analgesic in ethanol solvent[6] as described in the section "Reaction of Cyclohexene". Concerning the number of sulfonic acid groups, the thermogravimetric analyses (TGA-DTG) supported the above speculation. Figure 4 shows the TGA-DTG curves of the Amberlyst® 15, as-made 1% Pd/Amberlyst-15, and 1% Pd/Amberlyst-15 spent, that is, after the reaction under the conditions of entry 5 in Table 3 (the time-on-stream was 3 h from the first sampling). Each sample exhibited characteristic weight losses at *ca.* 90, 290, and 420 °C, which correspond to the desorption of H_2O/CO_2, $SO/H_2O/CO_2$, and $C_xH_y/NO/Cl$, respectively. The much smaller loss in mass around the temperature of 290 °C for the spent 1% Pd/Amberlyst-15 than for the as-made 1% Pd/Amberlyst-15 implied that the deterioration or decomposition of the sulfonic acid groups occurred during the reaction. Although the temperature of 1% Pd/Amberlyst-15 under the reaction conditions (95–120 °C) was below the maximum temperature recommended for the use of Amberlyst® 15 by Fluka (120 °C), the modification with palladium and the high pressure conditions might promote the thermal decomposition of the surface sulfonic acid groups even below 120 °C.[18] The greater loss in mass at *ca.* 420 °C after use of the catalyst in the reaction is attributed to the thermal decomposition of adsorbed reactant and products as well as the hydrocarbon moiety of Amberlyst® 15.

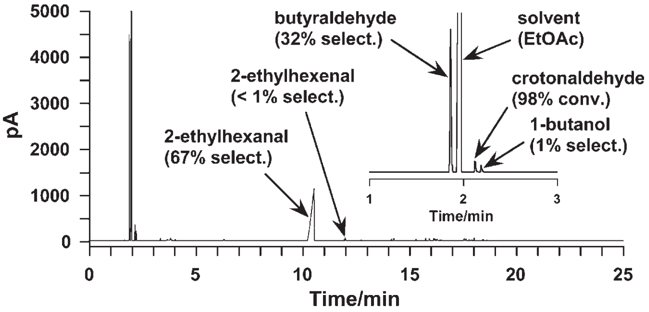


Figure 3. GC profile of the product sample obtained from the reaction of crotonaldehyde **10** under the conditions of entry 5 in Table 3. Column temperature conditions: 50 °C (10 min) → 20 °C min^{-1} → 250 °C (5 min). In the inset is shown a magnified view in the retention time range 1–3 min. Note that this is a sample without an internal standard substance. The peak of toluene (internal standard substance) appears at a retention time of *ca.* 3.30 min.

Table 4. Variation of the conversion and selectivity with time-on-stream in the reaction of crotonaldehyde **10** with H_2 in $scCO_2$ over 1% Pd/Amberlyst-15.[a]

Time-on-stream[b] [h]	Conversion[c] [%]	Selectivity[c] [%] **11**	**12**	**13**	**14**
1	>99	70	28	<1	1
5	>99	71	27	<1	1
7	99	67	32	<1	1
10	>99	60	39	<1	1
12	99	55	44	<1	1

[a] *Reaction conditions:* catalyst, 1.00 g; total pressure, 16 MPa; reactor temperature, 60 °C; flow rate of expanded gaseous CO_2, 1 L min^{-1}; flow rate of **10**, 0.3 mL min^{-1}; **10**:H_2 = 1:4.0.

[b] The time-on-stream started from the first sampling.

[c] Determined by GC.

The importance of the use of high-pressure CO_2 medium is obvious when one compares the result of entry 5 (total pressure: 16 MPa) with that of entry 6 (total pressure: 4 MPa) in Table 3. The retarded hydrogenations owing to the increased mass transport limitation of hydrogen led to poor results under the latter conditions, because the conversion and the selectivity to **11** were far lower, while the selectivity to **13** was much higher compared to those obtained under the conditions of entry 5. A similar tendency was already observed in the hydrogenation of cyclohexene; the hydrogenation rate decreased with decreasing the CO_2 pressure (see "Reaction of Cyclohexene" section).

The applied method may offer the following possible advantages to an industrial large-scale production process: (i) the separation of organic compounds (products and recovered reactant) from $scCO_2$ fluid can be easily performed by simple expansion of the

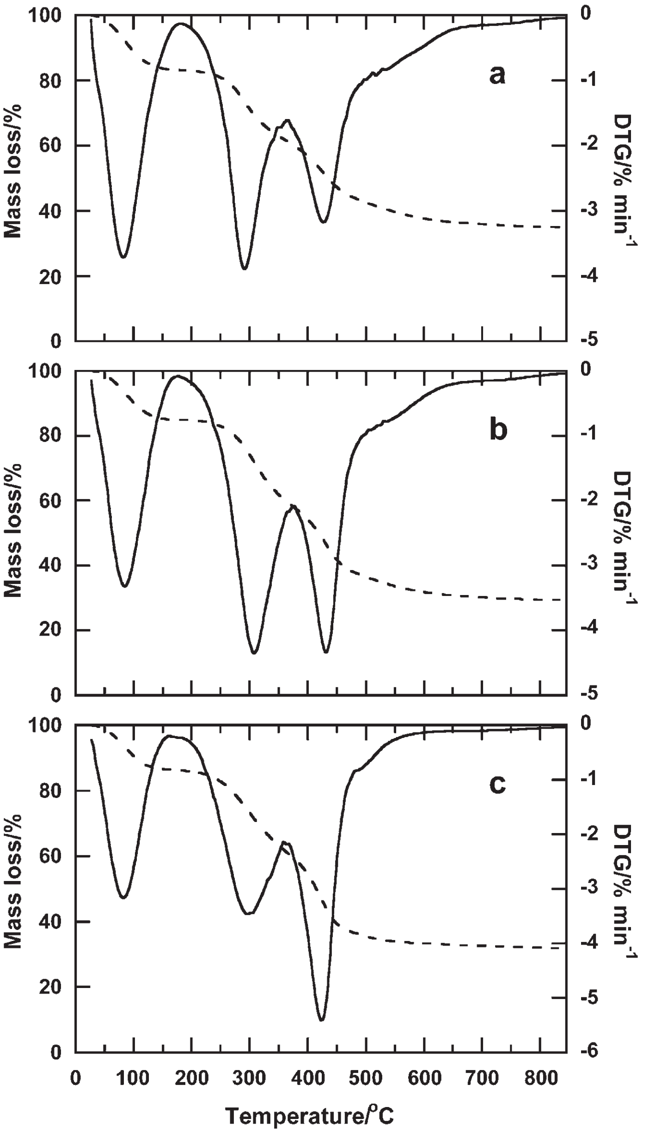


Figure 4. TGA-DTG curves of the Amberlyst® 15 (a), as-made 1% Pd/Amberlyst-15 (b), and 1% Pd/Amberlyst-15 spent in the reaction under the conditions of entry 5 in Table 3 (the time-on-stream was 3 h from the first sampling) (c). For analysis conditions, see "Catalyst Characterization" section.

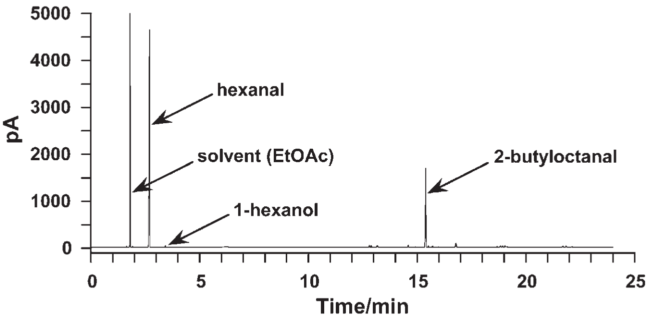


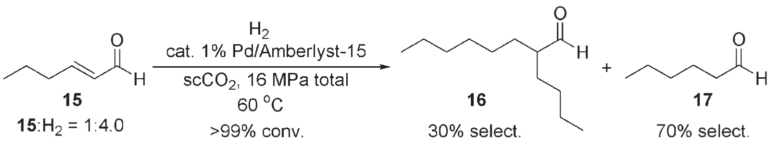
Figure 5. GC profile of the product sample obtained from the reaction of *trans*-2-hexenal **15** under the conditions described in the caption of Scheme 2. Column temperature conditions: 70 °C (10 min) → 20 °C min^{-1} → 250 °C (5 min). Note that this is a sample without an internal standard substance. The peak of toluene (internal standard substance) appears at a retention time of *ca.* 2.46 min.

reaction mixture; (ii) the only by-product, butyraldehyde, is also industrially important and easily separated from 2-ethylhexanal by distillation; (iii) a slight excess amount of hydrogen is sufficient to promote the one-pot reaction due to the great miscibility of hydrogen as well as crotonaldehyde in $scCO_2$; (iv) the one-pot reaction takes place satisfactorily at a low reactor temperature of 60 °C due to the rapid hydrogenations in $scCO_2$; (v) the catalyst exhibits a good long-term behavior and resists deactivation caused by the adsorption of reactant, products, CO_2, and by-products (e.g., water and oligomers); and finally (vi) crotonaldehyde containing stabilizers such as 2,6-di-*tert*-butyl-*p*-cresol and H_2O can be used owing to the catalyst's tolerance towards them.

Our approach has been successfully applied also to *trans*-2-hexenal **15** as shown in Scheme 2 and Figure 5. Thus under otherwise similar conditions, 2-butyloctanal **16** and hexanal **17** were obtained in 30 and 70% selectivity at quantitative conversion. The selectivity to the one-pot product **16** was lower compared with that to 2-ethylhexanal in the reaction of crotonaldehyde (Table 3, entry 5), presumably because the aldol condensation of **17** proceeds slower than that of butyraldehyde due to the increased steric constraints.

Structural Properties of 1% Pd/Amberlyst-15

The oxidation state of the catalysts was investigated using a specially constructed cell for X-ray absorption spectroscopy, which allows "*in situ*" observation of



Scheme 2. Application of 1% Pd/Amberlyst-15-$scCO_2$ catalytic system to the one-step production of 2-butyloctanal **16** from *trans*-2-hexenal **15**. *Reaction conditions:* catalyst, 1.00 g of 1% Pd/Amberlyst-15; total pressure, 16 MPa; reactor temperature, 60 °C; flow rate of expanded gaseous CO_2, 1 L min^{-1}; flow rate of **15**, 0.3 mL min^{-1}; **15**:H_2 = 1:4.0.

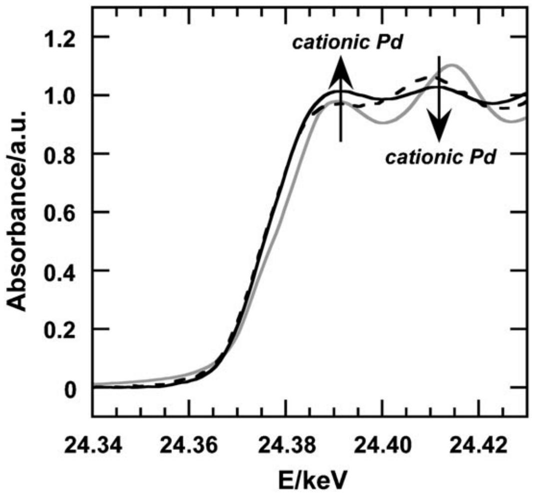


Figure 6. XANES spectrum of the pre-reduced 1% Pd/Amberlyst-15 (black solid line) and 1% Pd/C (black broken line), with the reference spectrum of Pd foil (solid gray line). For analysis conditions, see "Catalyst Characterization" section.

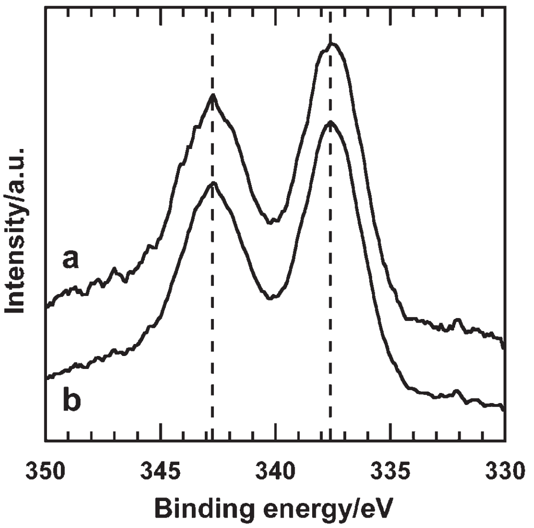


Figure 7. XPS spectra with Pd $3d_{5/2}$ and $3d_{3/2}$ lines for the as-made 1% Pd/Amberlyst-15 (a) and pre-reduced 1% Pd/Amberlyst-15 (b). For analysis conditions, see "Catalyst Characterization" section.

the catalysts during the reduction in a stream of hydrogen.[19] Figure 6 shows the X-ray absorption spectrum of 1% Pd/Amberlyst-15 and 1% Pd/C after the reduction at 100 °C for 1 h under a 5 vol% H_2/Ar flow in terms of X-ray absorption near-edge structure (XANES). The spectrum of Pd foil is also shown for comparison. As emerges from these spectra, most Pd atoms on 1% Pd/Amberlyst-15 as well as 1% Pd/C existed as metallic Pd(0). It is also noteworthy that the XANES spectrum of 1% Pd/Amberlyst-15 did not change before, during, and after the reduction with H_2, indicating that the palladium was virtually completely reduced during the preparation of the catalyst presumably by the reducing action of the ammonia ligand of the precursor complex $[Pd(NH_3)_4]Cl_2$.[5] Another interesting point is that the spectrum of 1% Pd/Amberlyst-15 implies the presence of some cationic palladium atoms on the particles.[20] This was confirmed also by X-ray photoelectron spectroscopy (XPS), which showed a shift of Pd $3d_{5/2}$ binding energy (BE) from 335.0 eV of metallic Pd(0) (Table 5 and Figure 7).[21]

Since acidic supports often enhance activity of the transition metals such as Pd and Pt for hydrogenations and hydrogenolyses, the interaction between the metal clusters and acidic supports has been examined in detail. Koningsberger and co-workers recently proposed that the increase in activity with increasing support acidity can be ascribed to an increase in the ionization potential of the metal particles directly induced by the Coulomb potential of the support oxygen ions of which electron density remarkably changes with the surface acidity.[22] Another possibility is the adsorption of a "support proton" onto the clusters, which results in the withdrawing of electron density from the surface Pd atoms.[23] We speculate that the oxygen atoms in sulfonic acid groups (i.e., S−**O**⁻ and S=**O**) and their protons are bonded to the Pd particles on 1% Pd/Amberlyst-15 through Coulomb interactions as shown in Figure 8. Such interactions are beneficial for firm immobilization of the Pd particles and also for the control of electron density on the surface Pd atoms. The electron deficiency of the surface Pd atoms should promote the adsorption of C=C bonds

Table 5. XPS data of the as-made and pre-reduced 1% Pd/Amberlyst-15.

C		N		O		S		Pd	
Atomic %	1*s* BE [eV]	Atomic %	1*s* BE [eV]	Atomic %	1*s* BE [eV]	Atomic %	2*p* BE [eV]	Atomic %	$3d_{5/2}$ BE [eV]
As-made sample									
60.9	284.6	3.1	401.9	30.0	532.1	5.8	168.8	0.15	337.6, 342.5
Pre-reduced sample[a]									
64.1	284.68	2.0	401.9	28.0	532.0	5.7	168.8, 164.0	0.20	337.6, 342.8

[a] The pre-reduction was performed at 100 °C for 1 h under a H_2/N_2 flow.

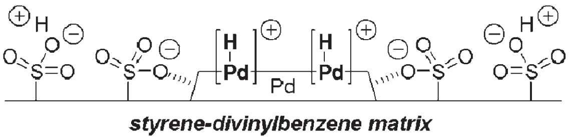


Figure 8. Surface model of 1% Pd/Amberlyst-15. The interaction of palladium particles with the sulfonic acid groups leads to immobilization of the particles as well as generation of several cationic surface Pd atoms.

and accelerate their hydrogenations, whereas it can suppress the hydrogenation of C=O bonds because the cationic Pd atoms would bond only to the oxygen atoms in C=O bonds, which results in unfavorable adsorption modes for the hydrogenations. The activity of 1% Pd/Amberlyst-15 was actually high and low for the hydrogenation of cyclohexene (see "Reaction of Cyclohexene" section) and benzaldehyde (see "Reaction of Benzaldehyde" section), respectively. As will be discussed in the next section, the Pd-attached proton species (denoted $[Pd_n\text{–}H]^+$) is considered to be the active "hybrid" site that can promote not only Pd-catalyzed reactions but also acid-catalyzed reactions.[23]

The possibility of the presence of small amounts of immobilized Pd(II) complexes formed by the reaction of $[Pd(NH_3)_4]Cl_2$ with sulfonic acid groups can virtually be ruled out because the XANES spectrum did not change before and after the reduction with H_2. In other words, the $[Pd(NH_3)_4]Cl_2$ complex is completely decomposed during the preparation step prior to the hydrogen treatment to form metallic palladium particles on the resin.

Figure 9 shows the transmission electron microscopy (TEM) image of the as-made and pre-reduced 1% Pd/Amberlyst-15, respectively. As the XANES spectrum suggested, metallic Pd particles already existed on the as-made 1% Pd/Amberlyst-15 even though it had not undergone the hydrogen treatment, demonstrating again that the precursor complex $[Pd(NH_3)_4]Cl_2$ is converted into metallic palladium during the preparation process by the action of the NH_3 ligand.[5] No significant change in Pd particle size was observed before and after the reduction. Powder X-ray diffraction (XRD) analysis also indicated the presence of metallic Pd particles on the as-made 1% Pd/Amberlyst-15 and no drastic change in the size after the reduction with H_2 (Figure 10). The Pd particle size estimated by the Scherrer formula was *ca.* 15 nm for both the as-made and pre-reduced 1% Pd/Amberlyst-15.

The surface properties of palladium particles were investigated using carbon monoxide as a probe molecule. The CO chemisorption assuming a stoichiometry of $CO:Pd_{surface}=1:1$ indicated that the dispersion of Pd metals for 1% Pd/Al_2O_3, 1% Pd/C, and 1% Pd/Amberlyst-15 were 21, 21, and 12%, respectively. Note that the average stoichiometry of the CO chemisorption was not the same for 1% Pd/Al_2O_3 and 1% Pd/Amberlyst-15, as the diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy investigations revealed. The spectra are shown in Figure 11. Since Amberlyst® 15 itself adsorbs a large amount of

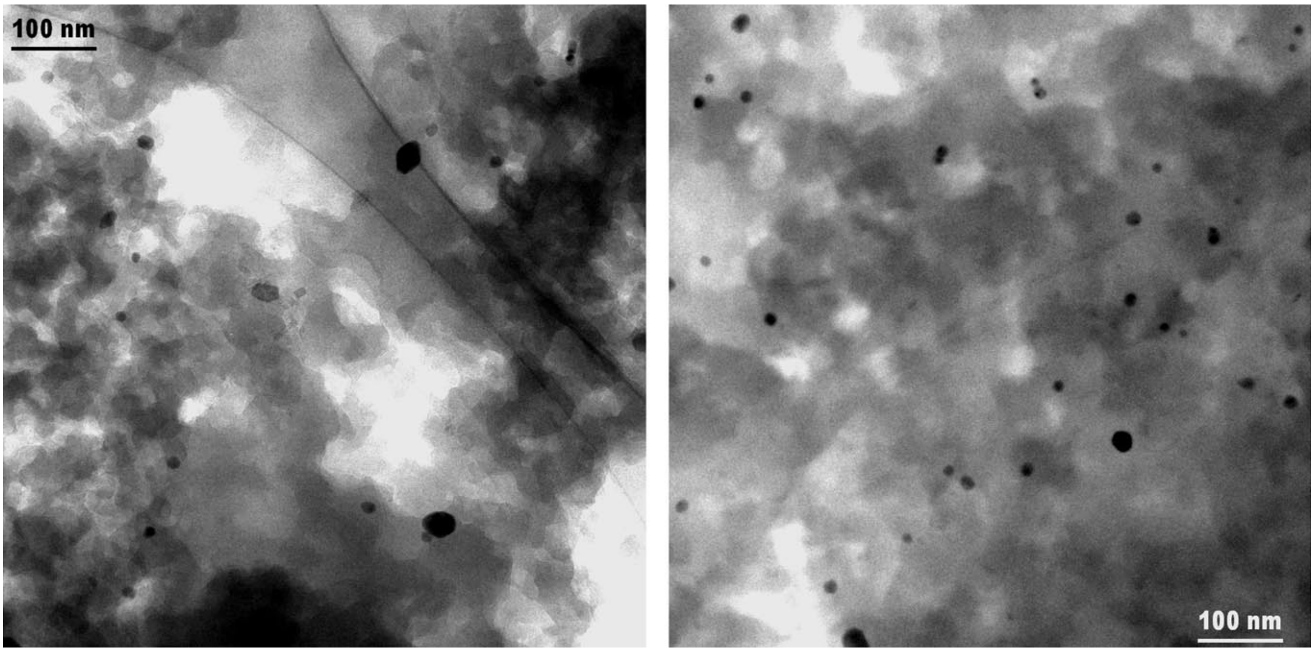


Figure 9. TEM image of the as-made (*left*) and pre-reduced 1% Pd/Amberlyst-15 (*right*). For analysis conditions, see "Catalyst Characterization" section.

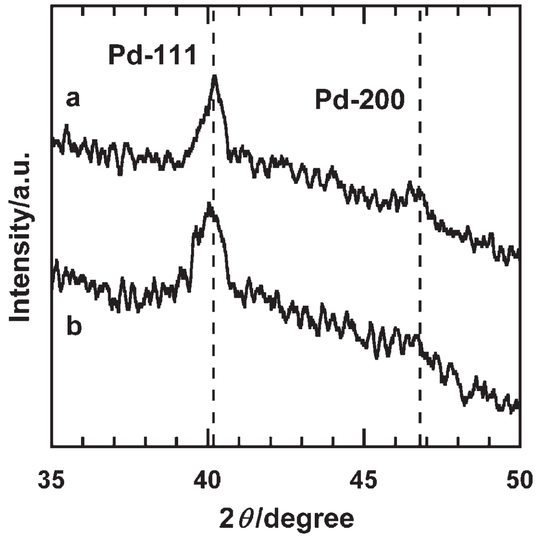


Figure 10. XRD pattern of the as-made (a) and pre-reduced 1% Pd/Amberlyst-15 (b). For analysis conditions, see "Catalyst Characterization" section.

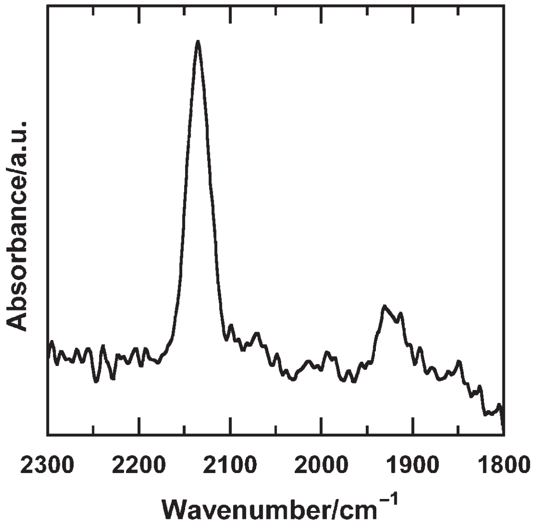


Figure 12. DRIFT differential spectrum between 1% Pd/Amberlyst-15 and Amberlyst® 15 after pre-reduction and subsequent exposure to CO. For analysis conditions, see "Catalyst Characterization" section.

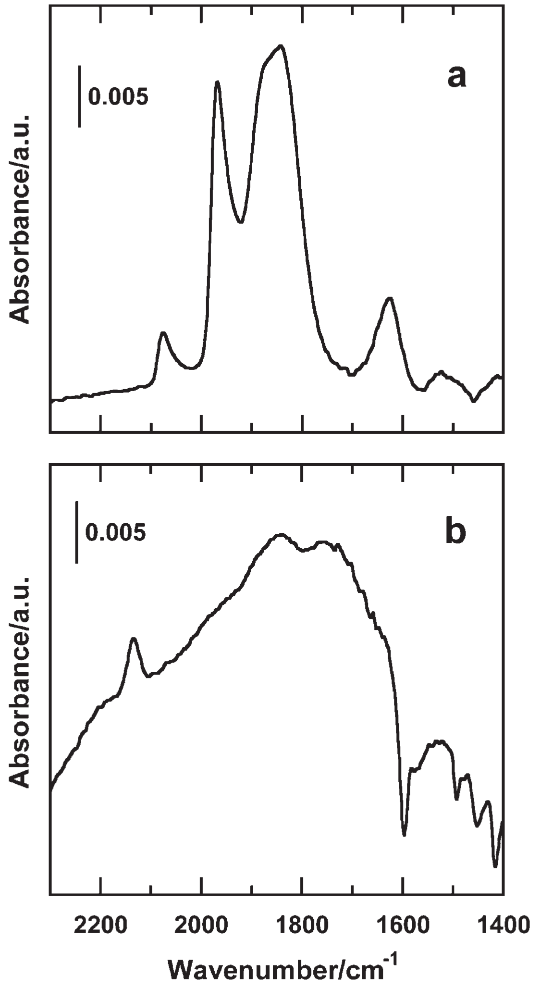


Figure 11. DRIFT spectrum of CO adsorbed on the pre-reduced 1% Pd/Al_2O_3 (a) and 1% Pd/Amberlyst-15 (b). For analysis conditions, see "Catalyst Characterization" section.

CO, the spectrum of CO-exposed Amberlyst® 15 was subtracted from that of CO-exposed 1% Pd/Amberlyst-15, which is shown in Figure 12. On 1% Pd/Al_2O_3, CO was adsorbed in both on-top (2100–2000 cm^{-1}) and bridge mode (2000–1700 cm^{-1}) in accordance with previous reports,[24] whereas the on-top CO was predominantly formed on 1% Pd/Amberlyst-15 (Figure 12; 2200–2100 cm^{-1}). Accordingly, the actual difference in metal dispersion between 1% Pd/Al_2O_3 and 1% Pd/Amberlyst-15 will be even larger than that obtained on the assumption of CO:$Pd_{surface}$ = 1:1. This behavior may be attributed to the presence of $[Pd_n–H]^+$ hybrid sites, which seems to be unfavorable for bridge CO adsorption. It is also noteworthy that the absorption band due to the on-top CO shifted to a higher wavenumber for 1% Pd/Amberlyst-15 compared to that of 1% Pd/Al_2O_3, indicating that the CO adsorption on 1% Pd/Amberlyst-15 was weaker than that on 1% Pd/Al_2O_3 owing to less electron transfer from metallic Pd to CO (back donation). A possible scenario is that the adjacent $[Pd_n–H]^+$ hybrid sites could withdraw electrons from the metallic Pd sites active for CO adsorption. Note that a similar IR band shift was observed also for CO adsorbed on the acidic zeolite NaHY-supported Pd catalyst.[23]

Summarizing the characterization results, it seems that the properties of palladium on Amberlyst® 15 are quite similar to those of palladium clusters on acidic zeolites, and consequently the notion established by Sachtler and co-workers,[23] namely the presence of $[Pd_n–H]^+$ hybrid sites, may be applicable also to the 1% Pd/Amberlyst-15.

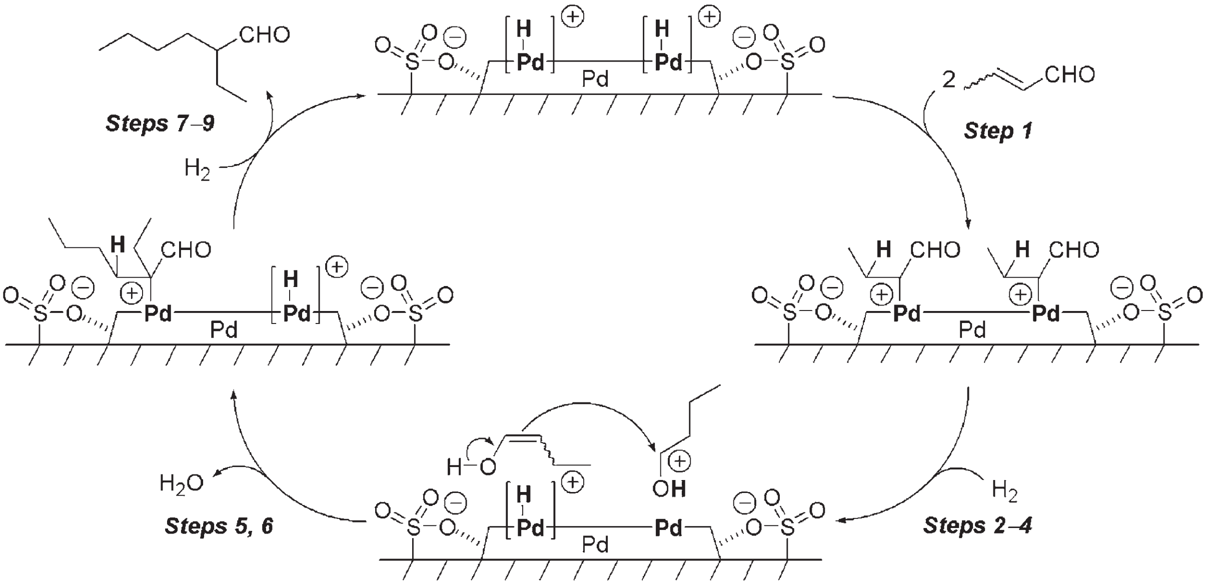
Mechanistic Consideration of the One-Pot Formation of 2-Ethylhexanal

The use of butyraldehyde **12** as starting compound led to the formation of many byproducts (see "Highly Efficient Continuous "One-Pot" Production of 2-Ethylhexanal from Crotonaldehyde" section), whereas such by-products are negligible when crotonaldehyde **10** was employed. During the reaction of **10**, however, a large amount of **12** was formed and the $scCO_2$ phase became almost similar to that when **12** was used as starting compound. Thus it can be speculated that **10** acts as poison or inhibitor for the undesirable side reactions as well as substrate during the reaction and therefore the clean conversion could be achieved.

A feasible reaction mechanism is shown in Scheme 3. During the reaction of **10**, the Pd sites and the "free" sulfonic acid groups that do not interact with the Pd particles should be blocked by the relatively strong adsorption of **10** on these sites, inhibiting their interaction with compounds other than **10** that can be the initial steps of the undesired byproduct formations. The multi-step reaction giving 2-ethylhexanal **11**, therefore, should not involve the desorption and re-adsorption step of the intermediates (i.e., **12**, 3-hydroxy-2-ethylhexanal, and 2-ethylhexenal) but take place in adsorbed manner throughout the reaction as depicted in Scheme 3. Here the notion of "$[Pd_n{-}H]^+$ adduct" proposed by Sachtler and co-workers seems to be important.[23] The adduct is a "hybrid" site that is able to function as metal and as acid site and thus can be the active sites for both hydrogenation and aldol condensation. The reactants and the reaction intermediates in the one-pot reactions can continually stay near the hybrid site until they are converted to the final products without shuttling between Pd and acid sites. We cannot, however, completely rule out the possibility that the "free" sulfonic acid groups participate in the catalysis.

Conclusions

The acidic resin (Amberlyst® 15)-supported palladium (Pd/Amberlyst-15) effectively promotes the continuous catalytic C=C bond hydrogenations in $scCO_2$ without affecting C=O bonds. In addition, owing to the metal-acid bifunctionality, the industrially important 2-ethylhexanal could be synthesized with this catalytic system in a one-pot pathway from crotonaldehyde *via* hydrogenation and aldol condensation. For these reactions, the use of $scCO_2$ is crucial because it lowers the gas-liquid mass transfer resistance and enhances the diffusion through the external fluid film of the catalyst. Under these conditions, the reactions proceed with satisfactory rate even at 60°C. The low temperature operation is attractive from an economical point of view. In addition, it can suppress undesirable side reactions and extend the lifetime of the thermally sensitive Pd/Amberlyst-15 catalyst. Actually, good long-term catalytic behaviors were observed for



Scheme 3. Plausible reaction mechanism for the one-pot production of 2-ethylhexanal **11** from crotonaldehyde **10**. Step 1, adsorption of **10**; step 2, H_2 adsorption with heterolytic bond cleavage; step 3, addition of hydride to the carbocation; step 4, acid-catalyzed keto-enol tautomerization (left) and proton addition (right); step 5, aldol condensation; step 6, adsorption of the condensate; step 7, H_2 adsorption with heterolytic bond cleavage; step 8, addition of hydride to the carbocation; step 9, desorption of **11**.

the hydrogenation of cyclohexene and the one-pot synthesis of 2-ethylhexanal.

Metal-acid hybrid sites, $[Pd_n{-}H]^+$ species, are speculated to be the active site for both hydrogenation and aldol condensation, promoting the one-pot synthesis of 2-ethylhexanal from crotonaldehyde. However, further work will be necessary to elucidate the role of these sites.

Experimental Section

Catalysts and Reagents

As a typical example, preparation method of 1% Pd/Amberlyst-15 is described in detail. The palladium precursor of $[Pd(NH_3)_4]Cl_2$ (ABCR, 99%; 0.0466 g, 0.190 mmol) and deionized water (20.0 g) were mixed in a 50-mL flask containing a stirring bar. After stirring the mixture for homogenization, Amberlyst® 15 (Fluka, 20–50 mesh, dry (moisture ~5%), product number: 06423, lot number: 1166065; 2.00 g) was added, and the resultant heterogeneous mixture was stirred at 80 °C for 24 h. The solid material was separated by filtration, washed with deionized water (15 mL), and dried at 100–110 °C overnight. The as-made material thus obtained already had metallic palladium on the surface (see "Structural Properties of 1% Pd/Amberlyst-15" section) presumably through the auto-reduction by the ammonia resulting from the decomposition of the tetramine complex.[5] Nevertheless, it was pre-reduced under an H_2/N_2 flow at 100 °C for 1 h just before the use for a catalytic reaction. The inductively coupled plasma-optical emission spectroscopy (ICP-OES) showed that the exact content of palladium in the pre-reduced 1% Pd/Amberlyst-15 was 0.80 wt%. For the synthesis of other supported transition metal catalysts, $[Pt(NH_3)_4]Cl_2{\cdot}H_2O$ (ABCR, 99%, 99.99% Pt), $[Ru(NH_3)_6]Cl_3$ (ABCR, 99%), and $RhCl_3{\cdot}3H_2O$ (Merck, 38% Rh) were used as metal precursors.

The following commercially available catalysts were employed in order to compare the catalytic performance of 1% Pd/Amberlyst-15 with those of conventional catalysts. 1% Pd/Al_2O_3 (Engelhard, 5376) and 1% Pd/C (Engelhard, 5109) were crushed and used as sieved fractions (*ca.* 0.5–1.4 mm).

Commercially available high-grade cyclohexene (Fluka, ≥99.5%, stabilizer: ~0.01% 2,6-di-*tert*-butyl-*p*-cresol), benzaldehyde (Aldrich, ≥99.5%, redistilled), butyraldehyde (Aldrich, ≥99.5%, redistilled), crotonaldehyde (Fluka, ≥99.5%, *cis*:*trans* = ~1:20, stabilizer: ~0.1% 2,6-di-*tert*-butyl-*p*-cresol and ~1% H_2O), and *trans*-2-hexenal (Acros, 99%) were used without further purification.

Continuous-Flow Reactor System and Reaction Procedures

Safety note: *The present experiments involve the use of relatively high pressures and require equipment with the appropriate pressure rating.*

The continuous-flow reactor system (NWA, Lörrach, Germany) employed in the present research is shown in Figure 13. Commercially available CO_2 (Pangas, 99.90%) and H_2 (Pangas, 99.995%) were used as received. The reactions were performed with a tubular reactor (designed by the ETH workshop) of which inner diameter and volume were 13 mm and 35 mL, respectively. Glass beads were placed above the catalyst to ensure an optimum flow distribution and mixing of the substrate at the entrance of the catalyst bed. Hydrogen was introduced through a 6-port switching valve (Rheodyne, model 7000) dosing 0.05 mL pulse at high pressure and constant frequency. Freshly opened liquid substrate was fed to the reactor using an HPLC pump (Gilson, model 305). The total pressure was

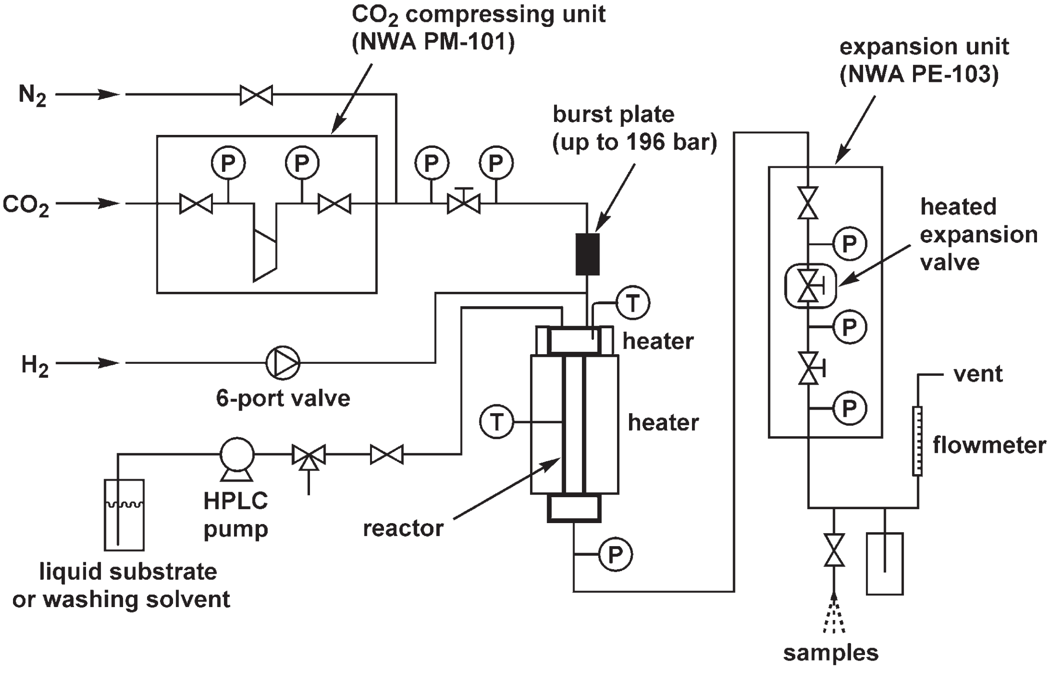


Figure 13. Schematic view of the continuous-flow high-pressure fixed-bed reactor system used in the present research.

adjusted to a constant value during the reactions with the pressure regulator connected to the CO_2 compressing unit and the total fluid flow was controlled at the expansion unit. The catalysts were first reduced in a stream of H_2/N_2 at 100 °C for 1 h in the reactor and stored under an N_2 atmosphere overnight. Then the stream of CO_2/H_2/substrate mixture was fed into the reactor to start the reaction.

The product samples, which were taken every 20 min, were collected in a glass vial containing a known amount of *n*-decane or toluene (internal standard substance). The mixture was subsequently diluted with ethyl acetate and subjected to GC analysis to determine the composition. A GC apparatus equipped with FID (Hewlett Packard, model HP 6890) that had an HP-5 column (J&W Scientific, 30 m × 0.32 mm × 0.25 μm) was used employing the following column temperature conditions: 50 °C (10 min) → 20 °C min^{-1} → 250 °C (5 min) for the reaction of butyraldehyde and crotonaldehyde; 70 °C (10 min) → 20 °C min^{-1} → 250 °C (5 min) for the reaction of cyclohexene, benzaldehyde, and *trans*-2-hexenal. After steady state conditions had been reached after *ca.* 3 h, conversion and selectivity were determined using the following equations. Average conversion and selectivity obtained from four samples were reported.

$$\text{Conversion (\%)} = \frac{\text{(mol of reactant reacted)}}{\text{(mol of reactant fed)}} \times 100$$

$$\text{Selectivity to a product (\%)} = \frac{\text{(mol of reactant converted to the product)}}{\text{(mol of reactant reacted)}} \times 100$$

The products were identified by comparing the GC retention times with those of commercially available authentic samples, GC-MS (Hewlett Packard, model HP 5973) with an analyzing program (Enhanced ChemStation, G1701BA, Version B.01.00, Hewlett Packard), and NMR spectroscopy. All the products described in this work are known compounds.

Phase Behavior Measurements

Visual observation of phase behavior under the reaction conditions was performed with a high-pressure view-cell which was designed similarly to a commercial screw-type manual pump (SITEC-Sieber Engineering, Switzerland).[25] Into the cell adjusted to 63 mL volume, cyclohexene **1** was introduced at room temperature, followed by the addition of gaseous H_2 and compressed liquid CO_2 in that order. The stirred mixture was heated up from room temperature to 60 °C and then the molar ratio of **1**:H_2:CO_2 in the cell was approximately 1:1.8:9.1 corresponding to the ratio of the flow rates (see caption of Figure 1). Under the conditions, the total pressure reached 11 MPa and the system was composed of gaseous and liquid phase. The total pressure was increased by introducing additional amounts of compressed liquid CO_2 with a constant cell volume of 63 mL to make the conditions similar to those of Figure 1.

Catalyst Characterization

TGA-DTG was performed on a STA 449 C thermoanalyzer (Netzsch) with an OmniStar mass spectrometer (Pfeiffer Vacuum) attached to the exhaust *via* heated Teflon and stainless steel lines (*ca.* 150 °C). Typically, 50 mg of the sample were placed in a crucible and heated in a stream of He (50 mL min^{-1}) from 30 to 850 °C with a heating ramp of 15 °C min^{-1}.

X-ray absorption spectroscopy was performed with a specially constructed *in situ* cell at a synchrotron laboratory (beamline X1, HASYLAB at DESY, Hamburg, Germany) using Si(311) double-crystal monochromator.[19] The pre-reduction of the samples was performed at 100 °C for 1 h in a stream of 5 vol% H_2/Ar. The spectra of the samples were recorded before, during, and after the reduction at room temperature, 100 °C, and room temperature, respectively.

X-ray photoelectron spectroscopy (XPS) was performed with an LHS11 MCD instrument (Leybold-Heraeus) using Mg Kα radiation. The pre-reduction of 1% Pd/Amberlyst-15 was then performed at 100 °C for 1 h under an H_2/N_2 flow. The sample was put on a sample holder, evacuated in a load lock to 10^{-6} mbar, and transferred to the analysis chamber of which the pressure was typically $< 10^{-9}$ mbar. The peaks were energy-shifted to the binding energy of Al 2*s* (118.5 eV) to correct for the charging of the material. The surface composition of the sample was determined from the peak areas that were computed after subtraction of the Shirley-type background by empirically derived cross-section factors.[26]

Powder X-ray diffraction (XRD) analysis was performed with a D5000 diffractometer (Siemens) using Cu Kα radiation in step mode between 15 and 65° 2θ with a step size of 0.01° and 0.3 s $step^{-1}$. The 1% Pd/Amberlyst-15 previously used in the CO chemisorption experiment (*vide infra*) was employed as the pre-reduced sample.

TEM investigations were performed on a Tecnai F30 microscope (FEI (Eindhoven); field emission cathode, operated at 300 kV). Then the pre-reduction of 1% Pd/Amberlyst-15 was performed at 100 °C for 1 h under a H_2/N_2 flow.

The CO chemisorption was carried out with an ASAP 2010 instrument (Micromeritics). The sample was flushed with He at 100 °C for 1 h, evacuated at the same temperature, and cooled down to 40 °C after which a leak test was performed. Then the sample was pre-reduced at 100 °C for 1 h in a stream of pure H_2 and then evacuated at the same temperature. Two isotherms, each composed of 11 points, were then measured at 40 °C. The first isotherm corresponded to the physisorbed and chemisorbed CO. After evacuation at 40 °C for 1 h, the second isotherm was measured, which corresponded to the physisorbed CO. From the difference between the two isotherms, the fraction of chemisorbed CO was determined. For the calculation of metal dispersion, a stoichiometric CO:$Pd_{surface}$ ratio of 1:1 was assumed and the exact Pd content of 0.80 wt% determined by ICP-OES was applied for 1% Pd/Amberlyst-15.

DRIFT spectra were recorded at room temperature with a resolution of 4 cm^{-1} using an EQUINOX 55 spectrometer (Bruker Optics) equipped with a liquid N_2-cooled MCT detector and an HVC-DRPZ reaction chamber (Harrick). Typically, 10 mg of sample diluted with 90 mg of KBr was pre-reduced at 100 °C for 1 h in a stream of 10 vol% H_2/Ar and cooled down to room temperature under pure Ar flow.

Then the flow was switched to 10 vol% CO/Ar for 45 min and subsequently to pure Ar for 45 min, followed by the IR measurement. Spectra were collected by adding 200 scans for 1% Pd/Al_2O_3 and 1000 scans for Amberlyst® 15 and 1% Pd/Amberlyst-15.

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