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Wacker-type oxidation in vapor phase using a palladium–copper chloride catalyst in a liquid polymer medium supported on silica gel

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ABSTRACT

Pd(II) chloride and Cu(II) chloride in various liquid polymer media supported on silica gel were prepared and used in a catalyst system for vapor-phase synthesis of acetaldehyde by Wacker-type oxidation of ethylene. This catalyst system supported on silica gel prepared by impregnation was quickly deactivated, while use of polyethylene glycol (PEG) as a liquid polymer medium supported on silica gel showed stable catalytic activity. PEG inhibited the formation of Pd metal particles, which deactivate the catalyst system. Addition of alkali metal salts, especially LiCl, to the $PdCl_2$–$CuCl_2$ catalyst system with PEG enhanced catalytic activity for 22 h, even when the Pd content was high, leading to high activity but poor stability. LiCl also inhibited the formation of metal particles.

1. Introduction

Acetaldehyde is industrially synthesized by Wacker-type oxidation of ethylene using a Pd–Cu catalyst system in liquid phase. Typically, the reaction is carried out in an aqueous solution of $PdCl_2$ and $CuCl_2$ used as co-catalysts. A drawback of this homogeneous catalyst system is that the catalyst is separated from the reaction mixture. Therefore, a reaction system using a solid catalyst would solve this problem. Several heterogeneous catalysts for ethylene oxidation have been reported [1–13], such as zeolites exchanged with Pd and Cu ions [2,3], Pd with vanadium-doped heteropolyacid [4–6], and Pd salt impregnated with vanadium oxide supported on alumina [7–9]. These catalysts serve as heterogeneous catalyst systems as well as halogen-free systems. Supported liquid phase catalysts (SLPCs) are known as heterogenized homogeneous catalysts and have properties of both heterogeneous and homogeneous catalysts. An SLPC is a homogeneous catalyst dissolved in a solvent with a high boiling point distributed in the pores of a porous support, and those for acetaldehyde synthesis have been investigated [10–13]. At first, a hydrochloric acid solution of $PdCl_2$ and $CuCl_2$ was simply loaded on alumina [11]. In this SLPC system, water evaporated during the reaction. To maintain the liquid phase, molten salts were used as the solvent and the catalyst in a later study because their vapor pressures were extremely low. KCl/CuCl as a molten salt was mixed with $PdCl_2$ and $CuCl_2$, and impregnated on silica as a catalyst for acetaldehyde synthesis, which showed high and stable catalytic activity [12].

Polymers are also candidates for supported liquid phases because their vapor pressure is low; some polymers are also used as solvents for metal complex catalysts. In our previous reports, polyethylene glycol (PEG) was shown to be an excellent liquid phase for SLPCs [14,15]. A tetraammineplatinum(II) chloride catalyst in PEG supported on silica gel [$Pt(NH_3)_4Cl_2$–PEG/SiO_2] was shown to be extremely active and stable for vapor-phase hydrosilylation of acetylene with trichlorosilane and trimethoxysilane. Furthermore, PEG is non-toxic, inexpensive, and readily available making it a suitable supported liquid-phase for SLPCs.

In acetaldehyde synthesis, $PdCl_2$ and $CuCl_2$ are requisite because a Pd(0) species reduced by ethylene is re-oxidized by a Cu(II) species to regenerate a Pd(II) species, i.e., contact between the Pd(0) and Cu(II) species is essential to continue the reaction. Thus, the SLPC concept is suitable for Wacker-type oxidation. In this study, PEG containing $PdCl_2$ and $CuCl_2$ was impregnated on silica gel, and this catalyst was used for ethylene oxidation. A highly active and stable catalyst consisting of a $PdCl_2$–$CuCl_2$–polymer system was developed for Wacker-type oxidation in the vapor phase, and was characterized by nitrogen adsorption and extended X-ray absorption fine structure (EXAFS) to explain its elevated and stable activity.

2. Experimental

2.1. Catalyst preparation

A typical catalyst was prepared as follows: Silica gel, Q-15 (surface area, 216 $m^2 g^{-1}$; pore volume, 1.27 $mL g^{-1}$; average pore diameter, 11 nm) obtained from Fuji Silysia Chemical Ltd. was dried at 200 °C for 24 h in an oven. $PdCl_2$ (>99.0%, Wako Pure Chemical

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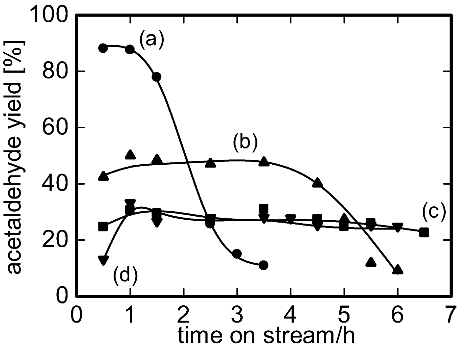

Fig. 1. Time evolution of acetaldehyde yield during oxidation of ethylene using $PdCl_2$–$CuCl_2$–PEG/SiO_2. PEG contents were (a) 0, (b) 10, (c) 20, and (d) 30% (w/w). The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.8 $\text{g}\,\text{h}\,\text{mol}^{-1}$. Pd and Cu contents were 6 and 3% (w/w), respectively.

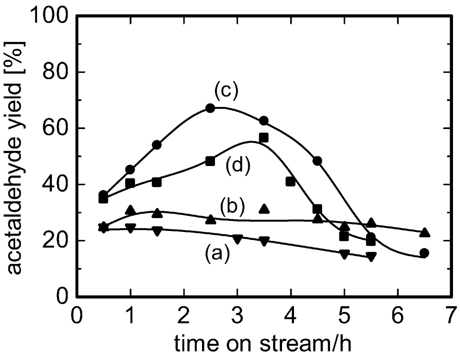

Fig. 2. Effect of Pd content on acetaldehyde yield in oxidation of ethylene using $PdCl_2$–$CuCl_2$–PEG/SiO_2. Pd contents were (a) 3, (b) 6, (c) 7.5, and (d) 9% (w/w). The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.8 $\text{g}\,\text{h}\,\text{mol}^{-1}$. Cu and PEG contents were 3 and 20% (w/w), respectively.

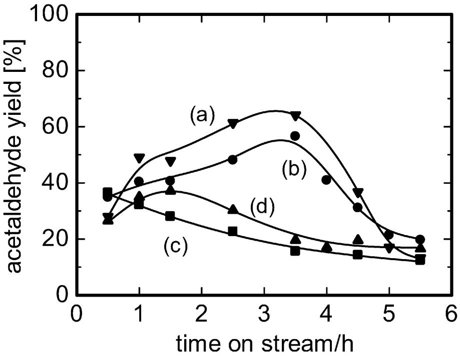

Fig. 3. Effect of Cu content on acetaldehyde yield in the oxidation of ethylene using $PdCl_2$–$CuCl_2$–PEG/SiO_2. Pd and Cu contents were (a) 9 and 6, (b) 9 and 3, (c) 2 and 6, and (d) 2 and 3% (w/w), respectively. The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.8 $\text{g}\,\text{h}\,\text{mol}^{-1}$. PEG content was 20% (w/w).

Industries), $CuCl_2$ (>99.0%, Kanto Chemical Co.), and PEG (average molecular weight 8200, Kanto Chemical Co.) were dissolved in 3 mL of deionized water, following which 1 g of dried silica gel was added and allowed to settle for 24 h. Finally, the catalyst was dried using a rotary evaporator. When an additive such as LiCl (>99.0%, Kanto Chemical Co.) was used, it also dissolved with $PdCl_2$, $CuCl_2$ and PEG in water.

2.2. *Reaction procedure*

The catalyst (0.86 g excluding PEG weight) was placed in a reactor tube (quartz; i.d., 15 mm) of a fixed-bed flow reactor system. In the case of ethylene oxidation, the catalyst was heated to 100 °C at an incremental rate of 2.5 $°\text{C}\,\text{min}^{-1}$ in a helium stream, following which ethylene (9 kPa), oxygen (36 kPa), and water (46 kPa) were fed to the reactor at 100 °C. The products were identified by gas chromatography-mass spectrometry and analyzed by gas chromatography. Yields of oxidation products were calculated based on ethylene fed to the reactor.

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$K\alpha$ with a MiniFlex (Rigaku Co.). XRD samples were not ground to avoid changes in the catalyst due to heat generated by grinding. EXAFS analysis was performed at the BL-7C facility of the Photon Factory at the High Energy Accelerator Research Organization, Japan, for Cu K-edge analysis. Pd K-edge absorption spectra were obtained at BL-10B and PF AR-10C.

3. Results and discussion

3.1. *Ethylene oxidation*

3.1.1. *Ethylene oxidation over $PdCl_2$–$CuCl_2$–PEG/SiO_2*

Fig. 1 shows time courses of acetaldehyde yield obtained from ethylene oxidation over catalysts with various PEG contents. In all cases, the main product was acetaldehyde, and the selectivity of carbon oxide and dioxide was low (<0.5%). The catalyst without PEG showed high activity at the beginning of the reaction; however, the yield rapidly decreased with time on stream. Addition of 10% (w/w) PEG improved catalytic stability. The yield was lower, and decreased after 5 h. When >20% (w/w) of PEG was used, slight deactivation was observed. SLPCs using PEG liquid showed stable activity.

The effects of Pd and Cu content were examined. Fig. 2 shows the effects of Pd content on acetaldehyde yield. The yield increased with increasing Pd content to 7.5% (w/w). However, use of 9% (w/w) Pd decreased catalytic activity, i.e., catalyst deactivation was observed when using >7.5% (w/w) of Pd. Cu content, on the other hand, did not affect catalytic activity. As shown in Fig. 3, when either 2 or 9% (w/w) of Pd was used, the time courses of acetaldehyde yield using different Cu contents were almost the same. This indicates that even 3% (w/w) Cu is excessive for continuing the redox cycle of Pd between (+2) and (0).

$PdCl_2$–$CuCl_2$–PEG/SiO_2 catalyst (Pd 6%, Cu 3%, PEG 20%), which showed stable activity, was examined using powdered XRD. Fig. 4 shows the XRD patterns of the catalyst before and after the reaction. Before the reaction, no peak was observed. This implies that $PdCl_2$ and $CuCl_2$ were highly dispersed in PEG. After the reaction, peaks assigned to Pd metal particles appeared, and their intensities increased with time on stream. In a Wacker-type reaction, redox of Pd is indispensable for continuing the reaction. Formation of Pd metal particles, which cannot be oxidized to Pd(II) ions, causes deactivation of the catalyst system. Thus, a slight deactivation of the $PdCl_2$–$CuCl_2$–PEG/SiO_2 catalyst (Pd 6%, Cu 3%, PEG 20%) system as shown in Fig. 1c is caused by the formation of Pd particles.

The $PdCl_2$–$CuCl_2$–PEG/SiO_2 catalyst system was also analyzed by EXAFS. Fig. 5 shows Pd K-edge EXAFS Fourier transforms of the catalysts before and after the reaction. In the as-synthesized cata-

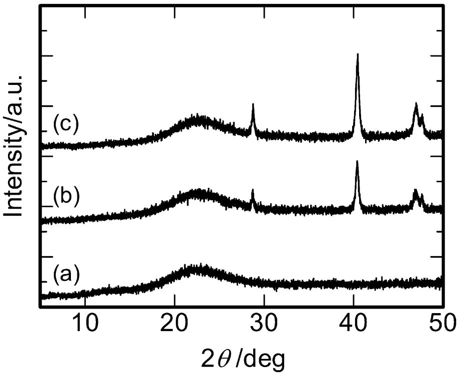

Fig. 4. X-ray diffraction patterns of $PdCl_2$–$CuCl_2$–PEG/SiO_2 (a) before reaction, and after reaction of (b) 4 h and (c) 7 h. Pd, Cu, and PEG contents were 6, 3, and 20% (w/w), respectively. The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.8 $\mathrm{g\,h\,mol^{-1}}$.

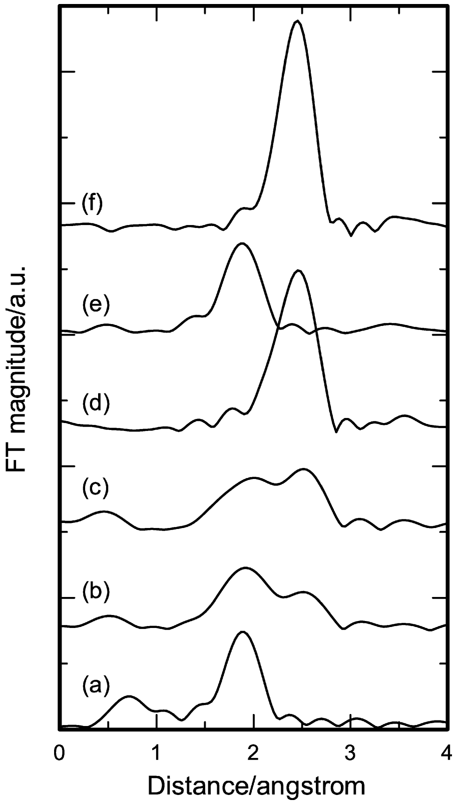

Fig. 5. Pd K-edge EXAFS Fourier transforms of $PdCl_2$–$CuCl_2$–PEG/SiO_2 catalysts before and after the reaction: (a) as-synthesized $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 20%), (b) $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 20%) after 1.5 h reaction, (c) $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 20%) after 5 h reaction, (d) $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 10%) after 5 h reaction, (e) $PdCl_2$, and (f) Pd foil. Pd and Cu contents were 6 and 3% (w/w), respectively. The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C.

lyst, a peak was observed at 1.8 Å (without phase-shift correction), and was the same as that in $PdCl_2$, indicating that a peak at 1.8 Å can be assigned to a Pd–Cl bond. After the reaction, the intensity of the Pd–Cl peak decreased with increasing time on stream, and a new peak at 2.5 Å appeared and became larger. This peak was assigned to a Pd–Pd bond. The formation of the Pd–Pd bond suggests the formation of Pd metal particles, which is consistent with XRD analysis. As shown in Fig. 1b, using 10% (w/w) PEG resulted in rapid deactivation of the catalyst. EXAFS analysis of the catalyst with 10% (w/w) PEG showed that the coordination number of the Pd–Pd bond was 10.3, which is close to the number for the Pd foil, 12. Moreover, this result suggests that aggregate Pd(0) causes deactivation.

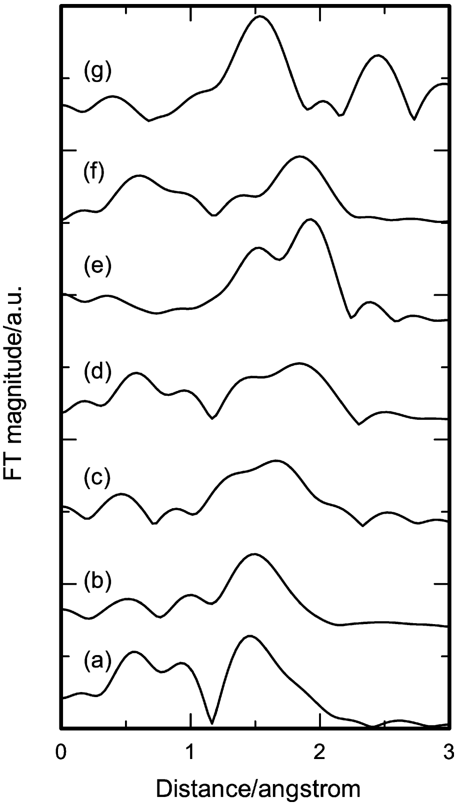

Fig. 6. Cu K-edge EXAFS Fourier transforms of $PdCl_2$–$CuCl_2$–PEG/SiO_2 catalysts before and after the reaction: (a) as-synthesized $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 20%), (b) $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 20%) after 1.5 h reaction, (c) $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 20%) after 5 h reaction, (d) $PdCl_2$–$CuCl_2$–PEG/SiO_2 (PEG 10%) after 5 h reaction, (e) $CuCl_2 \cdot 2H_2O$, (f) CuCl, and (g) CuO. Pd and Cu contents were 6 and 3% (w/w), respectively. The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C.

Cu K-edge EXAFS analysis was also performed. The results are shown in Fig. 6. The Cu species in the as-synthesized catalyst was similar to $CuCl_2$. During the reaction, several Cu species, which could not be assigned, were formed probably because various ligands such as OH, Cl, and H_2O were coordinated to Cu. As shown in Fig. 4, XRD analysis showed no crystalline particles of Cu compounds, and the Cu content did not affect the acetaldehyde yield (Fig. 3). These results strongly suggest that the decrease in catalytic performance with time is not caused by deactivation of the Cu catalyst.

3.1.2. Effects of promoters in $PdCl_2$–$CuCl_2$–PEG/SiO_2

As described in the previous section, use of PEG liquid improved catalytic stability; however, the acetaldehyde yield was low (around 25%) and slight catalytic deactivation was observed because of the formation of Pd metal particles. Thus, inhibition of contact among Pd metal atoms by the presence of another additive may lead to enhanced catalytic stability. Various alkali metal chlorides were used as additives when the Pd content was high, leading to high acetaldehyde yield but low catalyst stability. As shown in Fig. 7, addition of LiCl to the PEG medium increased the yield to 82%, and the yield remained high. Other chlorides showed low catalytic activity. Various lithium salts, bromide, nitrate, and acetate were also tested, as shown in Fig. 8. The nitrate showed high activity; however, slight deactivation was observed when using it. Thus, a combination of lithium and chloride ions is necessary for high and stable activity.

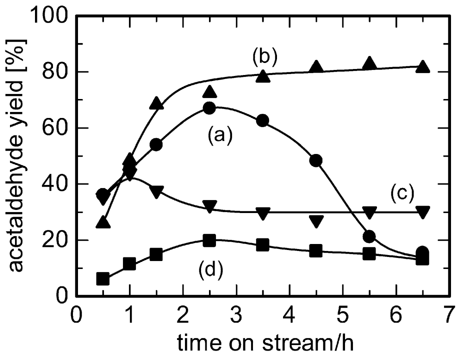

Fig. 7. Time evolution of acetaldehyde yield during oxidation of ethylene using $PdCl_2$–$CuCl_2$–PEG/SiO_2 with various alkali metal chlorides as promoters: (a) no additive, (b) LiCl, (c) NaCl, and (d) CsCl. The reaction was carried out at 8.5 kPa of ethylene, 36.1 kPa of oxygen, and 46.2 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.5 $\mathrm{g\,h\,mol^{-1}}$. Pd, Cu, and PEG contents were 7.5, 3, and 20% (w/w), respectively. Alkali metal/Pd = 1.21 ($\mathrm{mol\,mol^{-1}}$).

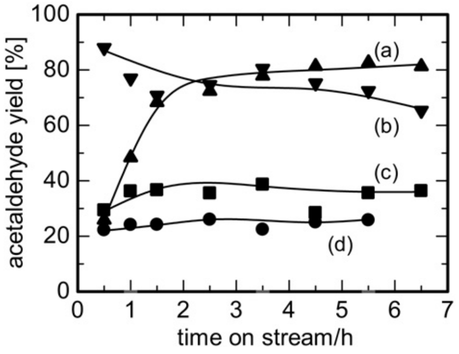

Fig. 8. Time evolution of acetaldehyde yield during oxidation of ethylene using $PdCl_2$–$CuCl_2$–PEG/SiO_2 with various additives: (a) LiCl, (b) $LiNO_3$, (c) LiBr, and (d) CH_3COOLi. The reaction was carried out at 8.5 kPa of ethylene, 36.1 kPa of oxygen, and 46.2 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.5 $\mathrm{g\,h\,mol^{-1}}$. Pd, Cu and PEG contents were 7.5, 3, and 20% (w/w), respectively. Alkali metal/Pd = 1.21 ($\mathrm{mol\,mol^{-1}}$).

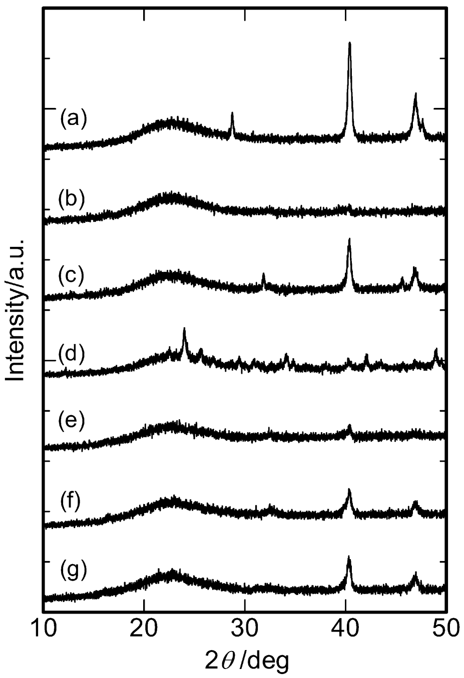

Fig. 9. X-ray diffraction patterns of $PdCl_2$–$CuCl_2$–PEG/SiO_2 after reaction of 6.5 h: (a) no additive, (b) LiCl, (c) NaCl, (d) CsCl, (e) LiBr, (f) CH_3COOLi, and (g) $LiNO_3$. The reaction was carried out at 8.5 kPa of ethylene, 36.1 kPa of oxygen, and 46.2 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.5 $\mathrm{g\,h\,mol^{-1}}$. Pd, Cu, and PEG contents were 7.5, 3, and 20% (w/w), respectively. Alkali metal/Pd = 1.21 ($\mathrm{mol\,mol^{-1}}$).

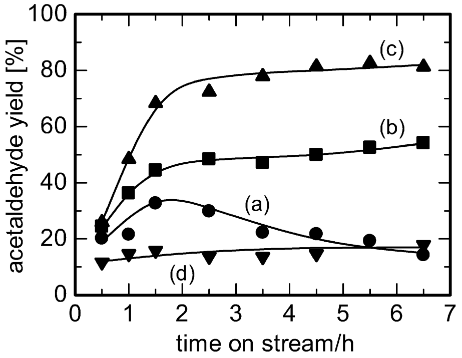

Fig. 10. Effect of LiCl content on acetaldehyde yield using $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2. LiCl content was Li/Pd = 0 (a), 1.0 (b), 1.21 (c), and 2.42 ($\mathrm{mol\,mol^{-1}}$) (d). The reaction was carried out at 8.5 kPa of ethylene, 36.1 kPa of oxygen, and 46.2 kPa of water at 100 °C using 0.86 g (excluding PEG weight) of the catalyst. The contact time, W/F, was 8.5 $\mathrm{g\,h\,mol^{-1}}$. Pd, Cu, and PEG contents were 7.5, 3, and 20% (w/w), respectively.

To clarify the role of LiCl, the catalyst used was examined by XRD analysis. Fig. 9 shows the XRD patterns of the catalysts with various chlorides after the reaction. Peaks due to Pd metal were observed in the catalysts with no additive or alkali metal salts except for LiCl, while there were no peaks in the pattern of the catalyst with LiCl. This result also indicates that the addition of LiCl inhibits the formation of Pd metal particles and leads to stable and high activity.

Addition of LiCl resulted in a long period of constant activity and high catalytic activity. The improvement in catalyst stability is probably caused by decreasing frequency of contact among Pd(0) complexes due to hindrance by Cl^- from LiCl, which is coordinated to Pd(0). $PdCl_2$ is known to be converted to Li_2PdCl_4 in the presence of LiCl [16]. The addition of LiCl leads to the formation of catalytically active $PdCl_4^{2-}$ complexes that are reduced to Pd(0) complexes with Cl^- ligands.

In Wacker-type catalysts, increased catalytic activity due to the addition of LiCl has been reported [17,18]. In these reports, the increase was caused by increased solubility of the Pd catalyst due to the formation of Li_2PdCl_4, and decreased potential for Pd(II)/Pd(0) coupling due to the addition of LiCl. These mechanisms are also plausible in our catalyst system. When LiBr was used as an additive, the acetaldehyde yield was lower than that when using LiCl. Br ions and Pd(II) also form Li_2PdBr_4, but the bond strength of Pd and Br is higher than that between Pd and Cl [19]. Strong coordination between Br and Pd(II) may hinder the coordination of ethylene to Pd. Moreover, in other Wacker-type reactions, a catalyst using Br ion showed lower activity [20,21]. Alkali metal chlorides other than LiCl are not easily dissolved in PEG because a polymer-salt complex is not formed in the case of NaCl or CsCl [22]. Thus, coordination of Cl^- to Pd cannot proceed very well, and consequently the catalyst system is deactivated.

The effect of LiCl content on catalytic activity was examined. When no LiCl was added, low activity occurred with a decline in the aldehyde yield (Fig. 10). Increasing LiCl content increased the yield; however, in the case of Li/Pd = 2.42 ($\mathrm{mol\,mol^{-1}}$), the yield was very low with no deactivation. XRD analysis of the catalyst system before and after the reaction indicated that Pd, Cu and Li compounds were dispersed in PEG even after the reaction. In homogeneous Wacker-type oxidation, the reaction rate is [1,17]

$$r = k\left[PdCl_4^{2-}\right][C_2H_4]\left[Cl^-\right]^{-2}\left[H^+\right]^{-1}.$$

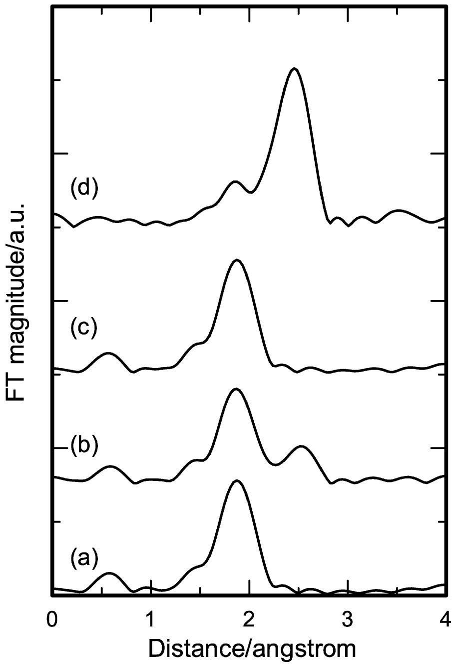

Fig. 11. Pd *K*-edge EXAFS Fourier transforms of $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2 catalysts before and after the reaction. $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2 (a) before and (b) after the reaction, $PdCl_2$–$CuCl_2$–PEG/SiO_2 (c) before and (d) after the reaction. The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen, and 48.0 kPa of water at 100 °C. Pd, Cu, and PEG contents were 7.5, 3, and 20% (w/w), respectively. Alkali metal/Pd = 1.21 ($mol\,mol^{-1}$).

Table 1
Coordination numbers (CN) and distances between Pd and Pd or Cl as derived from Pd *K*-edge EXAFS.[a]

Catalyst		Pd–Pd		Pd–Cl	
		CN	Distance (Å)	CN	Distance (Å)
Pd foil[b]	–	12	2.72	–	–
$PdCl_2$[b]	–	–	–	4	2.31
$PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2	before reaction	0	–	3.84	2.29
$PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2	after reaction	2.36	2.72	2.57	2.27
$PdCl_2$–$CuCl_2$–PEG/SiO_2	before reaction	0	–	3.75	2.29
$PdCl_2$–$CuCl_2$–PEG/SiO_2	after reaction	6.72	2.71	0.64	2.27

[a] The reaction was carried out at 9.6 kPa of ethylene, 33.3 kPa of oxygen and 48.0 kPa of water at 100 °C. Pd, Cu, and PEG contents were 7.5, 3, and 20% (w/w), respectively. Alkali metal/Pd = 1.21 ($mol\,mol^{-1}$).

[b] Reference samples.

In general, the reaction rate decreases with increasing Cl^- concentration. Therefore, excess content of LiCl over the amount of Cl^- required to form $PdCl_4^{2-}$ retards the reaction rate.

EXAFS analysis also revealed that addition of LiCl inhibits the formation of Pd metal particles. Fig. 11 shows Pd *K*-edge EXAFS Fourier transforms of $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2 before and after the reaction. After the reaction, a Pd–Pd peak was observed, but its intensity was small. On the other hand, in the case of the catalyst without LiCl, the intensity of the Pd–Pd peak was high. Coordination numbers and distances between Pd and Pd or Cl after curve fitting of the EXAFS data are summarized in Table 1. The coordination number of Pd–Pd increased to 6.7 after the reaction when LiCl was not added to the catalyst, whereas the addition of LiCl inhibited the increase in the coordination number. As mentioned above, XRD analysis showed no Pd metal particle formation in $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2; however, EXAFS analysis indicated that a small amount of Pd clusters or particles were formed.

A long-duration reaction was carried out over the catalyst showing the highest activity [Pd, Cu and PEG contents were 7.5, 3, and 20% (w/w), respectively, and the alkali metal/Pd was 1.21 ($mol\,mol^{-1}$)] to examine the stability of the catalyst. High yield (above 80%) was maintained for 22 h on stream, following which the yield gradually decreased. After the yield decreased, the XRD pattern of the catalyst showed the formation of Pd metal particles, which caused the deactivation. When the PEG content in the catalyst used was analyzed by thermogravimetry, 3 and 61% of the PEG charge was lost during the reaction lasting 6.5 and 40.5 h, respectively. The decrease in PEG content caused an increase in Pd concentration in PEG, leading to the formation of Pd metal particles. The vapor pressure of PEG (average molecular weight 8200) at 100 °C is very low according to a previous study [23]. Therefore, vaporization of PEG at the reaction temperature did not cause PEG loss. Moreover, after feeding of only O_2 to the reactor for 40 h, no loss of PEG in the catalyst was observed, indicating that oxidative degradation of PEG did not occur during the reaction. In acetaldehyde synthesis, HCl is formed as an intermediate and H_2O is required for synthesis. When HCl accumulated to some extent in the catalyst, hydrolysis of the ether in PEG probably started to form short-chain PEG, which has high vapor pressure and is easily lost.

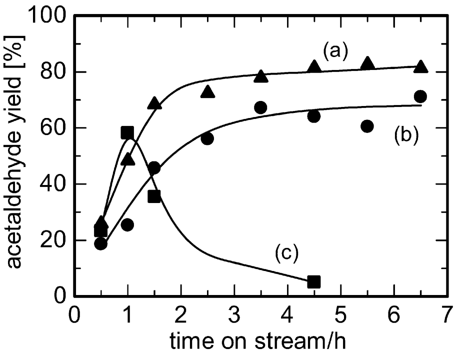

Fig. 12. Time evolution of acetaldehyde yield during oxidation of ethylene using $PdCl_2$–$CuCl_2$–LiCl/SiO_2 with various polymers. (a) PEG, (b) PPG, and (c) PVA. The reaction was carried out at 8.5 kPa of ethylene, 36.1 kPa of oxygen, and 46.2 kPa of water at 100 °C using 0.86 g (excluding polymer weight) of the catalyst. The contact time, W/F, was 8.5 $g\,h\,mol^{-1}$. Pd and Cu contents were 7.5 and 3% (w/w), respectively. Polymer volume was 182 $\mu l\,g_{SiO_2}^{-1}$. Alkali metal/Pd = 1.21 ($mol\,mol^{-1}$).

3.1.3. $PdCl_2$–$CuCl_2$–LiCl/SiO_2 with various polymers

Polypropylene glycol (PPG) and polyvinyl alcohol (PVA) were used instead of PEG for comparison at a volume of 182 $\mu l\,g_{SiO_2}^{-1}$. The results are shown in Fig. 12. PPG also improved catalytic activity and stability. Oxygen from PPG is probably also coordinated to Pd, Cu, and Li salts, and stabilizes them. However, the acetaldehyde yield was lower than that when using PEG. PPG is more hydrophobic than PEG, which may cause lower dispersion of the salts in the polymer. Use of PVA showed low activity and marked deactivation. In general, alcohols act as reductants. The hydroxyl group in PVA can reduce metal ions at a high temperature, leading to deactivation. Thus, PEG was the most suitable polymer for the catalyst system.

3.2. 1-Hexene and cyclohexene oxidation

Instead of ethylene, 1-hexene and cyclohexene were used for Wacker-type oxidation. Oxidation of 1-hexene gave only 2-hexanone, i.e., aldehyde was not formed. The time course of the 2-hexanone yield is shown in Fig. 13. In 1-hexene oxidation, $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2 showed high and stable activity. The product yield was lower than that in ethylene oxidation. On the other hand, no oxidized products were formed when using cyclohexene. These facts indicate that internal olefin is less reactive, which is consistent with a previous report [5].

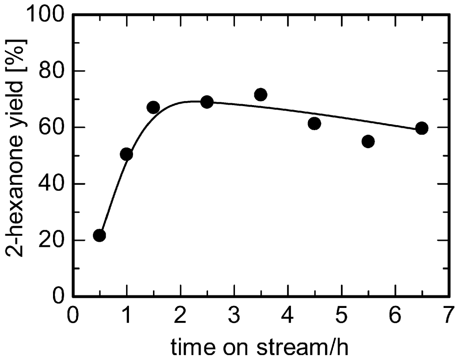

Fig. 13. Time evolution of 2-hexanone yield during oxidation of 1-hexene using $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2. The reaction was carried out at 8.5 kPa of 1-hexene, 36.1 kPa of oxygen, and 46.2 kPa of water at 100 °C using 0.86 g (excluding polymer weight) of the catalyst. The contact time, W/F, was 8.5 $\mathrm{g\,h\,mol^{-1}}$. Pd, Cu, and PEG contents were 7.5, 3, and 20% (w/w), respectively. Alkali metal/Pd = 1.21 ($\mathrm{mol\,mol^{-1}}$).

4. Conclusions

A catalyst system containing $PdCl_2$, $CuCl_2$, and LiCl dissolved in PEG supported on silica gel was developed as a new type of highly active and stable catalyst for Wacker-type oxidation. PEG and LiCl play a role in inhibiting the Pd particle formation that leads to deactivation of the catalyst. In Wacker-type oxidation, redox of Pd between (+2) and (0) is required to continue the reaction. Since the formation of Pd metal particles prevents this redox, the presence of PEG or LiCl inhibits Pd(0) from aggregating to the metal particles and yields an active and stable catalyst. $PdCl_2$–$CuCl_2$–LiCl–PEG/SiO_2 was stable for 22 h, and was active for 1-hexene oxidation to afford 2-hexanone.

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