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Easily separable molecular catalysis

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Abstract

Homogeneous metal catalysts offer greater selectivity and controllability because their molecular nature ensures that only one type of active site is present. However, the majority of large-scale, industrial chemical processes employs heterogeneous catalysts because of ease of their separation from products, thermal stability, and amenability to continuous processing. Heterogenization of homogeneous catalysts explores the cross-fertilization of two systems to combine most of their advantages. Some examples are discussed of heterogenized palladium complex catalysts applied for low-temperature CO oxidation, carbonylation for the synthesis of ibuprofen or naproxen, oxidative carbonylation for the synthesis of diphenyl carbonate, and functionalization of methane. There appears no significant change in reaction mechanisms when active centers are transferred from solution to the solid surface. In addition to the easy recovery, heterogenized homogeneous catalysts can have advantages in the productivity over homogeneous catalysts when a suitable support material is selected considering its hydrophilicity and surface reactivity.

Keywords: Heterogenized homogeneous catalysts; Palladium; CO oxidation; Carbonylation; Methane activation; Montmorillonite

1. Introduction

The majority of large-scale, industrial chemical processes employs heterogeneous catalysts because of ease of their separation from products, thermal stability, and amenability to continuous processing. However, homogeneous catalysts offer several advantages including the greater selectivity and controllability because their molecular nature ensures that only one type of active site is present. Heterogenization of homogeneous catalysts explores the cross-fertilization of two systems to combine most of their advantages. The heterogenization is typically done by immobilization or anchoring a soluble homogeneous metal complex to an inert support [1,55–62]. If the commonly encountered problem of metal leaching is avoided, the "hybrid" catalysts could provide unique opportunity in synthetic chemistry and chemical processing.

In this paper, several examples are presented from our works on heterogenization of palladium complexes which have been reported to be active for the low-temperature CO oxidation, carbonylation for the synthesis of ibuprofen and naproxen, oxidative carbonylation for the synthesis of diphenyl carbonate, and functionalization of methane. In all cases, active catalytic components were identified in homogeneous reaction catalyzed by soluble metal complexes and the components are immobilized on a suitable support. Metal complexes could be immobilized by the solid phase in several ways. Fig. 1 shows schematically a few of such methods. Ion exchange is the most common method of the immobilization but it has a major disadvantage of facile leaching of the metal complex into solution. Encapsulation of metal complexes by the ship-in-a-bottle method in intrazeolite

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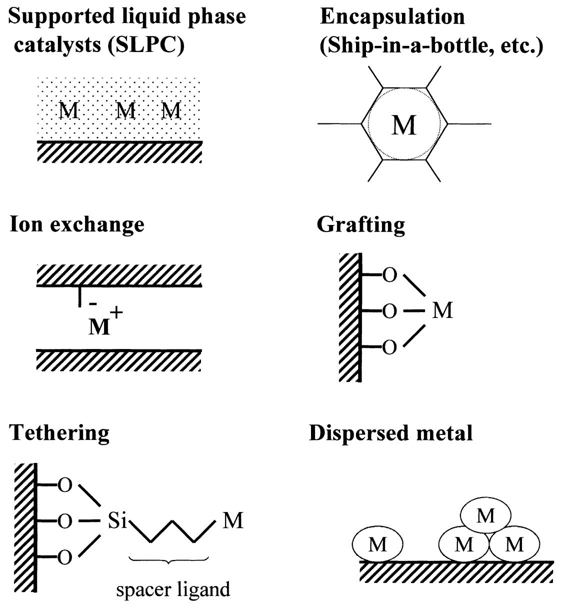

Fig. 1. Heterogenization (immobilization) of known homogeneous catalysts.

provides a more stable system because the complex, once formed, is too large to diffuse out [2,63,64]. In supported liquid phase catalysis (SLPC), very thin condensed liquid films may form on the surface of supports providing a homogeneous-like environment for a metal complex dissolved in the liquid film to catalyze the reaction. The grafting or tethering refers to the covalent attachment of metal complexes either directly (grafting) or via a spacer ligand (tethering) [3,65–67]. Supporting metal complexes on supports that do not contain specific anchoring sites form dispersed metal particles. These traditional supported metal catalysts are not expected to contain molecular catalytic species, but in some cases can show catalytic properties similar to those of homogeneous catalysts [4,68–71]. These preparation methods dictate not only the stability of heterogenized catalysts but also the degree of modification on the chemical nature of the metal complexes due to immobilization. Only a part of the methods of immobilization are covered in this article. The most significant omission is for catalysts employing zeolites or other molecular sieves as supports which should be covered by other papers in this proceeding.

2. Supported Wacker-type catalysts for low-temperature CO oxidation

Homogeneous $PdCl_2$–$CuCl_2$ catalyst known as Wacker catalyst has been applied to the partial oxidation of ethylene [5,6] and the low-temperature CO oxidation [7,8]. A number of attempts have been made to heterogenize this catalyst last few decades in order to facilitate catalyst recycle and to avoid the corrosive reaction mixture [9–29].

When activated carbon or alumina was impregnated with a solution of $PdCl_2$–$CuCl_2$ and dried below 373 K, the resulting catalysts were active in the gas phase CO oxidation at ambient conditions like $PdCl_2$–$CuCl_2$ dissolved in water provided that water was supplied continuously with the feed gases for the supported catalysts. Activated carbon was a preferred support because it gave a more active catalyst and pores of hydrophilic alumina were sometimes flooded with water [18–29]. On the other hand, silica-supported $PdCl_2$–$CuCl_2$ catalysts were rapidly deactivated during the reaction to become totally inactive [21,26]. XRD studies revealed that the dominant phase of copper was changed from $CuCl_2{\cdot}2H_2O$ into CuCl during a reaction in this deactivated catalyst [21,26]. However, the major phases of copper on carbon and alumina were Cu(II) species of $Cu_2Cl(OH)_3$ and $CuCl_2$. It can be interpreted that the reoxidation of reduced Cu(I) does not proceed and that reduced Pd(0) cannot be reoxidized into an active Pd(II) species over silica support. When the reaction temperature increased above 373 K, the hydrophilic alumina showed the higher rate for CO oxidation than the hydrophobic carbon support [26]. This means that the formation of a thin layer of aqueous phase is essential for this catalyst system. Low temperatures cause the pore-filling in the hydrophilic support and an inhibitory effect due to the difficulty of gaseous molecules to diffuse into the pores. However, at high temperatures, the formation of an aqueous layer can be achieved more easily over the hydrophilic support. Turnover frequencies (TOF) of CO oxidation at low temperatures are compared in Table 1. Carbon-supported Wacker catalysts showed TOF values comparable to those of the homogeneous Wacker catalyst. They are also comparable to those for oxide-supported gold catalysts [30], but much greater than those for supported platinum [31].

Table 1
TOF of CO oxidation over various catalysts

Catalyst	T (K)	TOF ($10^{-3}\,s^{-1}$)	Ref.	Remarks
$PdCl_2$–$CuCl_2$–$Cu(NO_3)_2$	295	20–55	8	Homogeneous catalyst
$PdCl_2$–$CuCl_2$/C	318	25	26	In wet condition
$PdCl_2$–$CuCl_2$–$Cu(NO_3)_2$/C	303	50	26	In wet condition
Au/Fe_2O_3	273	17–140	30	Based on Au surface area in dry condition
Pt/TiO_2	300	3–9	31	Based on Pt surface area in dry condition

Examination of the active catalysts with XAFS and XRD revealed that a molecular Pd(II) species with Cl ligand and solid $Cu_2Cl(OH)_3$ were active catalytic phases [22,23,29]. When copper was absent or present in an insufficient quantity, the Pd(II) species was reduced during the reaction and the catalyst was not active anymore for low-temperature CO oxidation. The $Cu_2Cl(OH)_3$ is formed by a reaction between $CuCl_2$ and the surface functional groups of the support and catalysts containing this copper species were more active than those containing $CuCl_2$. It appears that $Cu_2Cl(OH)_3$ is more efficient than $CuCl_2$in reoxidizing Pd(0) into Pd(II) in the catalytic cycle of the Wacker chemistry [29]. This is consistent with the report of Rouco [32] who showed that $Cu_2Cl(OH)_3$ was easier to reduce to cuprous species than $CuCl_2{\cdot}2H_2O$.

The addition of HCl in the feed stream decreased the catalytic activity [26]. The chemical environment around palladium probed by XAFS was not changed after the addition of HCl [29]. However, peaks representing $Cu_2Cl(OH)_3$ disappeared and strong peaks of $CuCl_2{\cdot}2H_2O$ appeared in XRD patterns [29]. This observation also supports that $Cu_2Cl(OH)_3$ is much more an active copper phase than $CuCl_2{\cdot}2H_2O$ and that the nature of copper phase is critical for the catalytic activity.

A significant improvement in catalytic activity was observed for carbon-supported Wacker-type catalysts when the carbon was treated with nitric acid [28] or $Cu(NO_3)_2$ was added as the second copper precursor in addition to $CuCl_2{\cdot}2H_2O$ [26]. The nitric acid treatment enriched hydrophilic functional groups on the carbon surface as shown by IR and temperature-programmed decomposition. It also promoted the formation of active copper phase, $Cu_2Cl(OH)_3$. These two factors contribute to an increase in the reaction rate for CO oxidation at a fixed relative humidity.

The promotional effect of $Cu(NO_3)_2$ reported for homogeneous $PdCl_2$–$CuCl_2$ [8] was also observed for carbon-supported Wacker-type catalysts [26]. Like the nitric acid treatment, the addition of $Cu(NO_3)_2$ as an additional copper source proved to enhance the hydrophilicity of carbon support and the formation of active copper phase, $Cu_2Cl(OH)_3$ [26,29]. There was an optimum mole ratio of $Cu(NO_3)_2/CuCl_2 = 2$ that yielded the maximum rate of CO oxidation and, at the same time, maximized the intensity of $Cu_2Cl(OH)_3$ peaks as observed by XRD. Furthermore, both solid phases of $CuCl_2{\cdot}2H_2O$ and $Cu_2Cl(OH)_3$ were observed before and during the reaction for carbon-supported $PdCl_2$–$CuCl_2$ while only well-developed $Cu_2Cl(OH)_3$ was found for carbon-supported $PdCl_2$–$CuCl_2$–$Cu(NO_3)_2$. Thus, it was clear that solid $Cu_2Cl(OH)_3$ was the most stable and active copper phase to sustain the catalytic cycle of Wacker chemistry. Indeed, a good correlation was observed between the reaction rates of CO oxidation and the XRD peak intensity of the $Cu_2Cl(OH)_3$ phase measured at different reaction and catalyst preparation conditions [26].

Effects of the amount of $CuCl_2{\cdot}2H_2O$ added in catalyst preparation were examined on the catalytic activity for CO oxidation and the structure and chemical state of palladium and copper in carbon-supported $PdCl_2$–$CuCl_2$ catalysts [29]. Reaction rates increased linearly with increasing amounts of $CuCl_2$ relative to $PdCl_2$ and seemed to be closely related to the structure of palladium. For those catalysts containing small amounts of $CuCl_2$ relative to that of $PdCl_2$, the coordination numbers of both Pd–Pd and Pd–Cl interactions appeared. Compared with the fresh catalyst, the coordination number of Pd–Pd increased whereas that of Pd–Cl decreased after the reaction. However, only Pd–Cl interaction was found when the mole ratio of $[CuCl_2]/[PdCl_2]$ was over 2. Therefore,

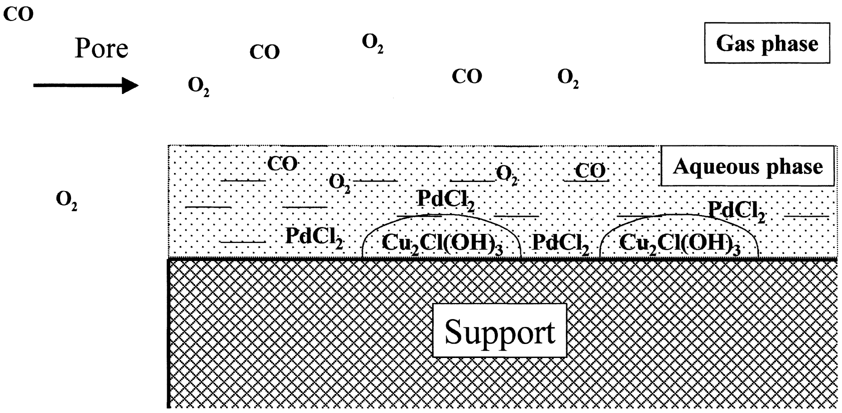

Fig. 2. A schematic model of the supported Wacker-type catalyst system.

the presence of $CuCl_2$ inhibits the partial reduction of $PdCl_2$ which is known to proceed by interaction with the surface acidic groups present on carbon support. Because only Pd–Cl interaction was found when the mole ratio of $CuCl_2/PdCl_2$ was over 2, however, the nature of palladium species only cannot explain the continuously increasing catalytic activity with increasing $CuCl_2/PdCl_2$ ratios even above 2. Cu K-edge XANES spectra revealed that the majority of copper compounds was present as Cu(II) species before the reaction. However, some of these Cu(II) compounds appeared to be reduced to Cu(I) species after the reaction at 303 K when $CuCl_2/PdCl_2$ ratio was small. As the amount of $CuCl_2$ increased, the peak representing Cu(I) compounds was weakened and disappeared entirely when the mole ratio became 10. This result implies that the reoxidation of reduced cuprous ion by dioxygen is the rate-determining step in the overall CO oxidation process and a larger amount of $CuCl_2$ than the stoichiometric value is in need.

The supported Wacker-type catalyst system belongs to supported liquid phase catalysis (SLPC) depicted in Fig. 1 [33]. However, a little modification should be incorporated for this supported Wacker-type catalyst discussed here. Solid copper phase, $Cu_2Cl(OH)_3$, plays a major role as shown in a catalyst model depicted in Fig. 2. The system could be viewed as a combined homogeneous–heterogeneous system because, in addition to the solid support, one active metal component (copper) remains in a solid phase. A possible reaction mechanism is shown schematically in Fig. 3. It is the same as the traditional Wacker chemistry in the liquid phase except that the solid copper phase is involved as the redox partner of palladium as in the case of the Pd/V_2O_5 system described by Evnin et al. [9] for ethylene oxidation.

Unlike other low-temperature CO oxidation catalysts, the supported Wacker catalyst system proved to be stable in the presence of water and organic halogen compounds and has been successfully applied to LTCRC (low-temperature catalytic removal of carbon monoxide) process to treat the vent gas from a terephthalic acid plant after a pilot test [27].

3. Hydrocarboxylation for the synthesis of ibuprofen and naproxen over palladium–anchored montmorillonite

1-(4-isobutylphenyl) propionic acid (ibuprofen, IBPA), an important nonsteroidal anti-inflammatory drug, can be synthesized via an elegant three-step process from isobutyl benzene. This process developed by Hoechst–Celanese is composed of acylation, hydrogenation, and carbonylation [34]. Another important nonsteroidal anti-inflammatory drug, 6-methoxy-2-methyl-2-naphthalene acetic acid (naproxen) can also be manufactured in the same manner from 6-methoxy naphthalene. For the last step of carbonylation, homogeneous palladium complexes have been reported to be active [35–37]. To heterogenize this homogeneous palladium complex, various

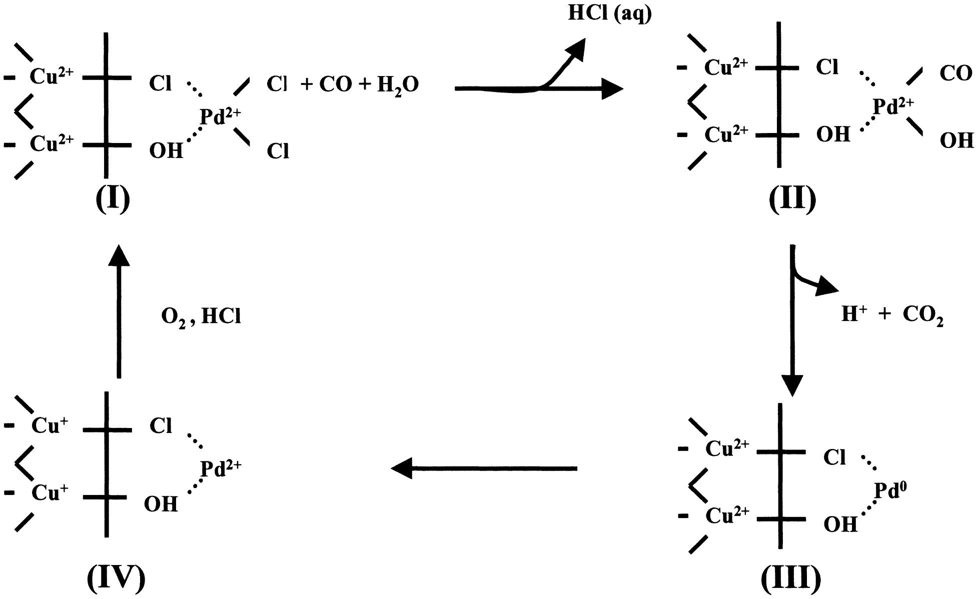

Fig. 3. A proposed reaction mechanism for CO oxidation over the supported Wacker-type catalyst system.

supported palladium catalysts have been prepared and tested as shown in Table 2 [38]. Alumina-supported palladium catalysts could not catalyze the carbonylation reaction and produce a large amount of oligomers. On the other hand, carbon-supported palladium catalysts showed high conversion of 1-(4-isobutylphenyl) ethanol (IBPE) and produced remarkable amounts of desired branched 1-(4-isobutylphenyl) propionic acid (IBPA(B)) with small amounts of linear 1-(4-isobutylphenyl) propionic acid (IBPA(L)). A problem with the carbon support was the facile hydrogenation to give 4-isobutylphenyl ethane (IBE) [38]. Compared with these two kinds of supported palladium catalysts, palladium complex anchored on montmorillonite, showed a catalytic behavior much closer to that of the homogeneous system showing a high conversion of IBPE and an excellent selectivity for IBPA(B). Under the same reaction conditions, the heterogenized catalyst showed a similar activity and a better selectivity to ibuprofen than the

Table 2
Hydrocarboxylation of IBPE with the homogeneous $PdCl_2$ catalyst and heterogenized palladium catalysts[a]

Catalyst	IBPE conversion (%)	Selectivity (%)				
		IBE	IBPCl	IBS	IBPA(B)	IBPA(L)
$PdCl_2$[b]	100	0	0	0	98.0	2.0
3.3% Pd/montmorillonite[b,c]	98.1	0	6.3	1.4	92.3	0
5% Pd/C[d]	99.9	25.6	0.1	1.0	77.0	0
5% Pd/Al_2O_3[d,e]	34.6	0	0.4	68.6	0	0
5% Pd/SiO_2[d]	77.6	0	4.8	94.5	0.8	0

[a] Pd = 0.2 mmol, PPh_3 = 0.13 g, IBPE = 5 g, 3-pentanone = 81 ml, 5% HCl = 10.0 g, temperature = 398 K, reaction time = 13 h.
[b] CO pressure = 50 atm.
[c] Palladium precursor = $(C_6H_5CN)_2PdCl_2$, silane ligand = $(C_2H_5O)_3Si(CH_2)_3NH_2$.
[d] CO pressure = 40 atm.
[e] The remaining 31% was the dimer.

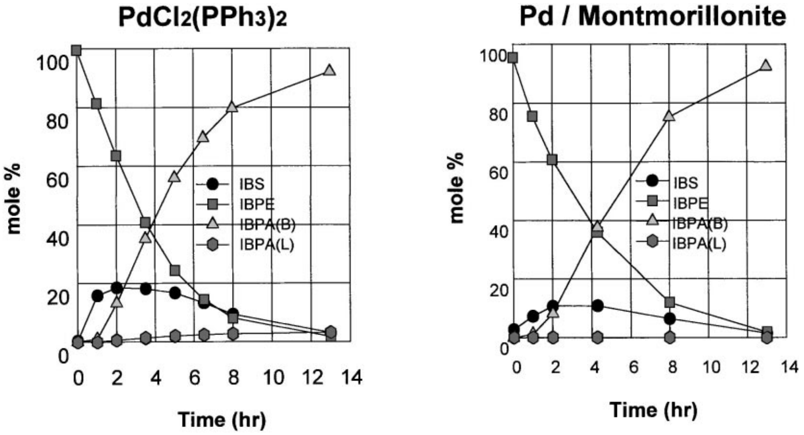

Fig. 4. The time course of the hydrocarboxylation for the homogeneous $PdCl_2(PPh_3)_2$ catalyst and the heterogenized Pd–anchored montmorillonite catalyst. Reaction condition: $IBPE = 5.0\,g$, $PPh_3 = 0.13\,g$, $5\%\,HCl = 10\,g$, $temperature = 398\,K$, $CO\,pressure = 40\,bar$, $time = 13\,h$, $P/Pd = 2.2$, $(C_2H_5O)_3Si(CH_2)_3NH_2$, $(C_6H_5)_2PdCl_2$.

homogeneous counterpart because 4-isobutyl styrene (IBS) and 1-(4-isobutylphenyl) ethyl chloride (IBPCl) formed over Pd/montmorillonite could be further converted to the desired IBPA(B). For the synthesis of Pd/montmorillonite, H-montmorillonite was first exchanged with a silane and then complexed with Pd ion to obtain an anchored Pd catalyst. The catalyst required the presence of PPh_3 and HCl in the reaction solution even if $PPh_3$and chlorine ion had already been coordinated to the Pd precursor during preparation [38].

The time courses of the hydrocarboxylation are compared in Fig. 4 for homogeneous and heterogeneous catalysts. Except for concentrations of intermediates, the nature of intermediates and changes of their concentrations with time were strikingly similar. This suggests that the reaction proceeds by a similar reaction mechanism for both homogeneous and heterogeneous catalysts. Considering the behavior of other supported catalysts shown in Table 2, the molecular nature of active catalytic species in Pd/montmorillonite appears responsible for this similarity. The catalyst recovered after a batch of the reaction showed the activity similar to that of the fresh catalyst for a new batch of the reaction and thus could be recycled [38].

Similar results were obtained for the synthesis of naproxen over the same Pd/montmorillonite as shown in Table 3. However, unlike in ibuprofen synthesis, the heterogeneous catalyst was less effective than the homogeneous counterpart in selectivity for naproxen synthesis mainly because of the significant forma-

Table 3
Hydrocarboxylation of α-(6-methoxy-2-naphthyl) ethanol with the homogeneous $PdCl_2$ catalyst and heterogenized palladium catalysts[a]

Catalyst	Time (h)	Conversion (%)	Selectivity		
			6-Methoxy-2-ethyl-naphthalene	6-Methoxy-2-vinyl-naphthalene	Naproxen
$PdCl_2$	15	100	0	8.3	91.7
3.3% Pd/montmorillonite[b]	15	100	12.3	4.3	83.4
5% Pd/C	13	100	36.9	6.9	53.9
5% Pd/Al_2O_3	19	75.6	4.7	43.5	3.6
5% Pd/SiO_2	22	86.4	1.9	98.1	0

[a] $Pd = 0.45\,mmol$, $PPh_3/Pd = 2.2$, $substrate = 2.5\,g$, $1,4\text{-dioxane} = 40\,ml$, $10\%\,HCl = 0.5\,g$, $H_2O = 2.0\,g$, $temperature = 373\,K$, $CO\,pressure = 50\,bar$.

[b] Palladium precursor = $(C_6H_5CN)_2PdCl_2$, silane ligand = $(C_2H_5O)_3Si(CH_2)_3NH_2$.

Table 4
Effects of support on DPC yields over supported Pd catalysts[a]

No.	Pd catalysts	% Pd dispersion	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
1	5% Pd/C	49.5	30.3	69.5	21.1
2	5% Pd/Al_2O_3	50.5	12.5	60	7.5
3	5% Pd/SiO_2	39.0	19	50	9.5
4	5% Pd/MgO	8.3	9	53.5	4.8

[a] Reaction conditions: catalyst, 1.02 g (0.48 mmol); $Ce(OAc)_3$, 0.48 mmol; Bu_4NBr, 1.3 mmol; Benzoquinone, 2.4 mmol; phenol, 0.53 mol; $P_{co} = 77$ bar; $P_{O_2} = 5.8$ bar; $T = 381$ K; 7 h reaction.

tion of the hydrogenated product, 6-methoxy-2-ethyl naphthalene.

4. Oxidative carbonylation of phenol to diphenyl carbonate over supported palladium catalysts

Oxidative carbonylation of phenol to produce diphenyl carbonate (DPC), an intermediate for non-phosgene polycarbonate synthesis, was investigated in a multi-step electron transfer system containing homogeneous and heterogeneous Pd as the main catalytic component [39–50]. The overall reaction stoichiometry is shown in Eq. (1).

$$C_6H_5OH + CO + \tfrac{1}{2}O_2 \rightarrow C_6H_5OCOOH_5C_6 + H_2O \qquad (1)$$

$Ce(OAc)_3$ was adopted as a metal cocatalyst together with Bu_4NBr and benzoquinone as additives. Screening tests for the proper support have been conducted to show that carbon support gave the higher yield of DPC than other supports such as silica and alumina even though Pd dispersions were almost same (Table 4) [50]. Furthermore, carbon-supported Pd catalyst showed a better DPC yield than the best homogeneous system with $Pd(OAc)_2$ for the same amount of total Pd [50]. For the fixed total amount of Pd in the reaction system, the lower the loading of palladium in Pd/C, the higher yield of DPC was obtained even though Pd dispersions were almost the same [50].

In DPC synthesis, one equivalent mole of water per DPC is produced and it is considered to be an inhibitor for DPC synthesis. Therefore, the reduced population of water around palladium over hydrophobic carbon appears responsible for the higher DPC yields for Pd/C compared with hydrophilic supports such as silica and alumina, and homogeneous catalysts. Addition of activated carbon into the $Pd(OAc)_2$-catalyzed homogeneous catalyst system improved the DPC yield, but not up to the level of Pd/C catalyst system (Table 5). Thus, it seems important to carry out the reaction in the hydrophobic carbon pores. For Pd/C catalysts, the carbon with more surface functional groups gave a lower DPC yield, which could be considered as another indication that the hydrophobicity of the support was important. For carbon supports with the same surface property, the smaller size of palladium now gave the higher yield of DPC.

The XRD analysis showed that Pd remained in the metallic state throughout the reaction. Any soluble

Table 5
DPC yields for the homogeneous $Pd(CH_3COO)_2$ catalyst and the heterogeneous Pd/C catalyst[a]

No.	Pd catalyst (0.36 mmol)	Additives	PhOH conversion (%)	DPC selectivity (%)	DPC yield (%)
1	$Pd(OAc)_2$	–	25.7	49.9	12.8
2	5% Pd/C	–	35.8	60.25	21.5
3	$Pd(OAc)_2$	AC (0.72 g)	26.0	65.0	16.0
4	–	–	16.0	15.0	2.4
5	–	AC (1.0 g)	24.0	29.0	7.0

[a] Reaction condition: $Co(OAc)_2$, 0.36 mmol; Bu_4NBr, 10.0 mmol; benzoquinone, 1.85 mmol; phenol, 0.39 mol; $P_{co} = 77$ bar; $P_{O_2} = 5.8$ bar; $T = 381$ K; 12 h reaction.

Table 6
CF_3COOCH_3 yields for the homogeneous $PdCl_2$ catalyst and heterogeneous Pd/C catalysts[a]

Run	Pd catalyst	Particle size,[b] d (nm)	CF_3COOCH_3 (M)
1	$PdCl_2$ (homogeneous)	–	0.31 (0.22[c])
2	5% Pd/C (473 K)	6.5	0.31 (0.19[c])
3	5% Pd/AC (673 K)	12.6	0.26
4	5% Pd/AC (873 K)	36.6	0.19
5	5% Pd/AC (1073 K)	75.9	0.17

[a] 5% Pd/C, 21.5 mg (Pd, 1.0×10^{-5} mol) or $PdCl_2$ (1.0×10^{-5} mol); $Cu(OAc)_2$ (5.0×10^{-5} mol), NaCl (1.5×10^{-4} mol); H_2O, 1 ml; CF_3COOH, 3 ml; CH_4, 300 psi; N_2, 100 psi; CO, 200 psi; O_2, 100 psi; 100°C; after 10 h reaction.

[b] By X-ray line broadening.

[c] After 5 h reaction.

palladium could not be detected in the ICP analysis (with the detection limit less than 1 ppm) of the filtrate of the reaction mixture after the reaction, indicating that dissolution of palladium into the reaction solution was, if there was any, negligible. From these results, we can conclude that the most active catalyst should be a finely dispersed metallic palladium supported on the hydrophobic material.

5. Oxidation of methane to a methanol derivative over supported palladium catalysts

As shown in Table 6, carbon-supported Pd with a Cu compound is an active catalyst for the oxidation of methane to a methanol derivative CF_3COOCH_3 in the presence of CO, O_2 and CF_3COOH [51,52]. The yield of the methanol derivative increases with the amount of a Cu compound containing chloride ion [52]. The yield of CF_3COOCH_3 increases with the amount of chloride ion supplied as NaCl at a fixed amount of $Cu(OAc)_2$. This appears to be closely related to the structural change of palladium. In the absence of a Cu compound, the particle size of the metallic palladium determined by XRD increased after a reaction [52]. Even in the presence of a Cu compound, this agglomeration of palladium was observed in the absence of chloride ion. As the amount of chloride ion increases, the coordination number of Pd–Pd decreases and that of Pd–Cl increases as determined in Pd K-edge EXAFS curve fitting (Table 7). In the presence of chloride ion, copper species were reduced into CuCl [51,52]. From XRD and XAFS analysis, it was found that most active catalyst contained both Pd(II) and Pd(0) and that the formation of Pd(II) was promoted by a Cu compound and chloride ion [52]. The Pd(II) species coordinated with chloride ion appeared to be essential for the selective functionalization of methane and metallic Pd for the in situ generation of H_2O_2 from CO, H_2O, and O_2. A proposed general reaction scheme is shown in Fig. 5. The role of a Cu compound containing chloride ion is the oxidation of the bulk metallic

Table 7
Results of Pd K-edge EXAFS curve fitting for carbon-supported Pd catalysts

No.	$[Cu(CH_3COO)_2]/[Pd]$	[NaCl]/[Pd]	Shell	N	σ^2 (Å^2)	R-factor
1[a]	0	0	Pd	7.1	0.0074	0.0018
2[b]	0	0	Pd	8.7	0.0058	0.0026
3[b]	5	0	Pd	9.2	0.0062	0.0023
4[b]	5	5	Pd	7.7	0.0059	0.0020
			Cl	0.3	−0.0032	
5[b]	5	15	Pd	1.5	0.0044	0.0052
			Cl	3.0	0.0051	

[a] Before reaction.

[b] After reaction R-factor gives a sum-of-squares measure of the fractional misfit, which is defined as $R = \frac{\sum_{i=1}^{N}\{[\mathrm{Re}(fi)]^2+[\mathrm{Im}(fi)]^2\}}{\sum_{i=1}^{N}\{[\mathrm{Re}(\tilde{\chi}_{\mathrm{data}_i})]^2+[\mathrm{Im}(\tilde{\chi}_{\mathrm{data}_i})]^2\}}$.

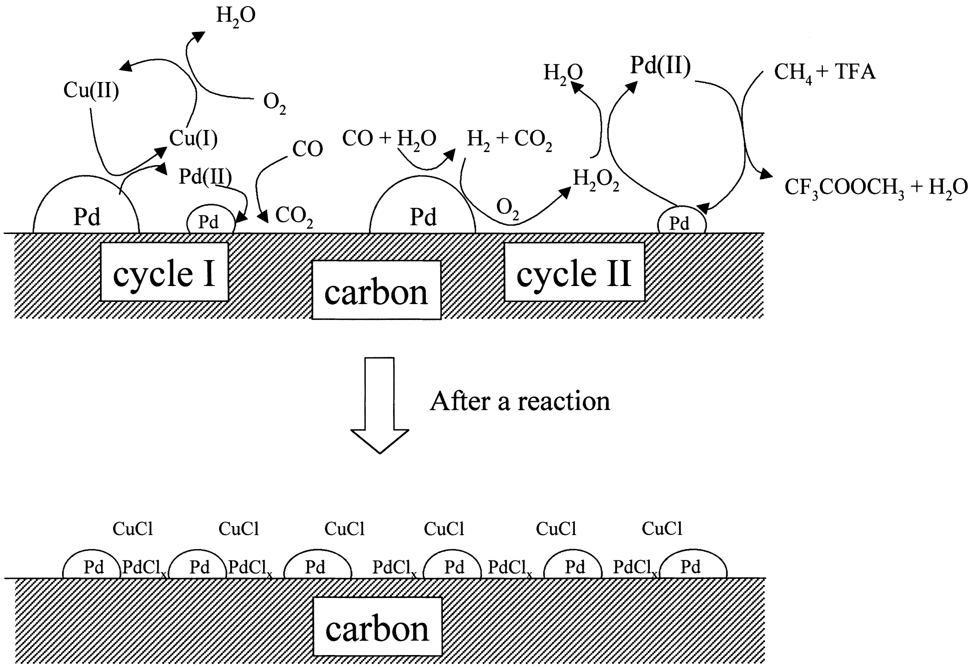

Fig. 5. A proposed reaction scheme for the functionalization of methane over Pd/C catalyst and the second metal system.

palladium into Pd(II) species coordinated with chloride ion as observed in Wacker chemistry (cycle I). This process inhibits the agglomeration of palladium metal and stabilizes the finely dispersed palladium. The in situ generated H_2O_2 plays a major role in functionalization of methane with a Pd(II) complex (cycle II).

H_2O_2 can also be generated from H_2 and O_2 over supported palladium catalysts [53]. Thus, H_2/O_2 was introduced instead of $CO/H_2O/O_2$ for the same catalysts. There were significant differences between the two systems as shown in Table 8. In the case of $CO/H_2O/O_2$ system, the homogeneous catalyst ($PdCl_2$–$CuCl_2$) showed almost the same yield of the methanol derivative as the heterogeneous catalyst (Pd/C–$CuCl_2$). On the other hand, in the case of H_2/O_2 system, the heterogeneous catalyst (Pd/C–$Cu(CH_3COO)_2$) gave a much higher yield of the methanol derivative than the homogeneous catalyst ($Pd(CH_3COO)_2$–$Cu(CH_3COO)_2$). Most of homogeneous palladium complexes precipitated during the reaction for the homogenous system. However, in situ

Table 8
Comparison of CF_3COOCH_3 yields between $CO/H_2O/O_2$ and H_2/O_2 systems[a]

Temperature (K)	Yield of CF_3COOCH_3 (mmol)			
	CO[b]		H_2[c]	
	$PdCl_2$	Pd/C	$Pd(CH_3COO)_2$	Pd/C
333	0.09	0.09	0.08	0.48
353	0.74	0.63	0.08	0.78

[a] Pd, 0.010 mmol; H_2 (or CO), 100 psi; CH_4, 500 psi; O_2, 100 psi; after 5 h reaction.
[b] $CuCl_2$, 0.050 mmol; TFA, 4 ml; H_2O, 1 ml.
[c] $Cu(OAc)_2$, 0.050 mmol; TFA, 4 ml; TFAA, 1 ml.

formation of H_2O_2 from H_2 and O_2 might be more favorable when starting from the heterogeneous Pd catalyst. Unlike $CO/H_2O/O_2$ system, the presence of chloride ion has an inhibitory effect on the catalytic activity in H_2/O_2 system [54]. This may also reflect the different requirements for balancing Pd(II) and Pd(0) sites needed for an efficient functionalization of methane.

6. Conclusions

Heterogenization of the known homogeneous catalysts could be accomplished in various ways that could stabilize molecular catalytic species on a solid surface. Thus, easily separable molecular catalysts could be devised. There appears no significant change in reaction mechanisms when active centers are transferred from solution to the solid surface. The hydrophilicity and surface reactivity of the support are important variables in determining catalytic performance of heterogenized catalysts. Under favorable conditions, the presence of both support and catalyst can have beneficial synergistic effects. XAFS was found to be a powerful technique to characterize these heterogenized homogeneous catalysts.

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