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MALDI TOF Mass Study on Oligomerization of $Pd(OAc)_2(L)_2$ (L = Pyridine Derivatives): Relevance to Pd Black Formation in Pd-Catalyzed Air Oxidation of Alcohols

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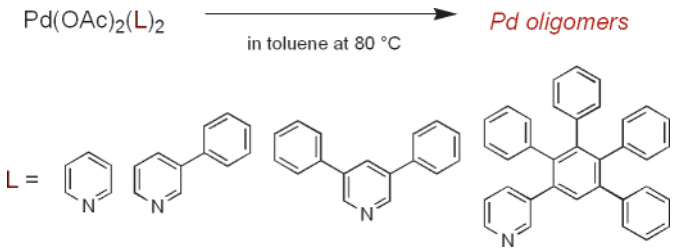
ABSTRACT



Oligomerization of $Pd(OAc)_2(L)_2$ (L = pyridine derivatives), a catalyst for the air oxidation of alcohols, is studied with MALDI TOF mass, using dithranol as the matrix. The degree of the Pd oligomerization is influenced by the pyridine ligands, and this ligand effect is similar to one observed for Pd black formation in the catalysis.

In homogeneous transition metal catalysis,[1] aggregation of the metal center is a serious problem leading to decreased catalytic activity and selectivity.[2] In particular, homogeneous Pd catalysts are known to aggregate easily and Pd black formation (extreme case of aggregation) prevails, even though Pd catalysts are very useful and widely employed.[3] Recently, we found that palladium acetate bearing 3-(2,3,4,5-tetraphenylphenyl)pyridine (3-Ph_4PhPy) as the ligand, Pd-$(OAc)_2$(3-Ph_4PhPy)$_2$, is a good catalyst and successfully suppresses the Pd black formation in the air oxidation of alcohols, while the corresponding Pd acetates with pyridine (Py), 3-phenylpyridine (3-PhPy), and 3,5-diphenylpyridine (3,5-Ph_2Py) as the ligand result in complete Pd black formation (Scheme 1).[4]

Concerning catalytically inactive species in homogeneous catalysis, there have been few spectroscopic studies even though they are indispensable in exploring highly active catalysts. Recently, catalytically inactive Pd dimers and trimers were studied by time-resolved UV−vis spectra.[5] However, higher oligomerization of catalyst resulting in Pd black formation has never been observed. In this letter, we utilize MALDI TOF mass for the first time to examine oligomer formation of $Pd(OAc)_2(L)_2$ (L = Py, 3-PhPy, 3,5-

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(2) van Leeuwen, P. W. N. M. *Appl. Catal., A* **2001**, *212*, 61−81.
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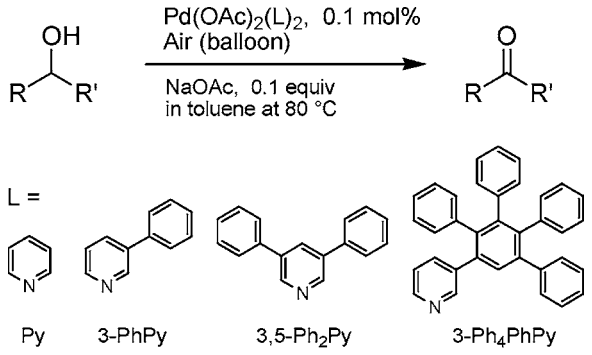
Scheme 1



Ph_2Py, and 3-Ph_4PhPy) as an early stage of Pd black formation (catalyst deactivation).

A toluene solution of $Pd(OAc)_2(L)_2$ (0.002 M, the same concentration as in the catalytic reaction[4]) was heated at 80 °C for 3 min and cooled to room temperature with stirring for 5 min, which afforded a pale yellow solution without any Pd black formation. Heating for a longer time caused the Pd black formation and much more complicated MALDI TOF mass spectra were obtained. A mixture of the heated $Pd(OAc)_2(L)_2$ solution (100 μL) and a dithranol (as a matrix) solution (100 μL, 8 mg/mL in toluene) was vigorously shaken for 10 s. Then, a small aliquot (0.7 μL) of the mixture was applied on a target plate. The MALDI TOF mass spectra (Figure 1) were measured on a Bruker Autoflex with the linear positive mode. MALDI TOF mass measurements employing another matrix,[6] such as 2,5-dihydroxybenzoic acid, α-cyano-4-hydroxycinnamic acid, and 5-chlorosalicylic acid, as well as ESI and FD mass measurements with the same sample provided almost no mass peaks. Thus, the MALDI TOF mass measurement with dithranol as the matrix is especially effective for examining the Pd oligomers.

In Figure 1, there are several kinds of peaks marked as a, b, c, α_x, β_y, and γ_z. Among them, the peaks a, b, and c are assigned to the Pd mono- and dinuclear species: $Pd(OAc)(L)_2$, $Pd_2(OAc)_2(L)$, and $Pd_2(OAc)_2(L)_2$, respectively, where L is Py, 3-PhPy, 3,5-Ph_2Py, or 3-Ph_4PhPy. The observed *m*/*z* values of the peaks a, b, and c vary with L (Figure 1a−d),

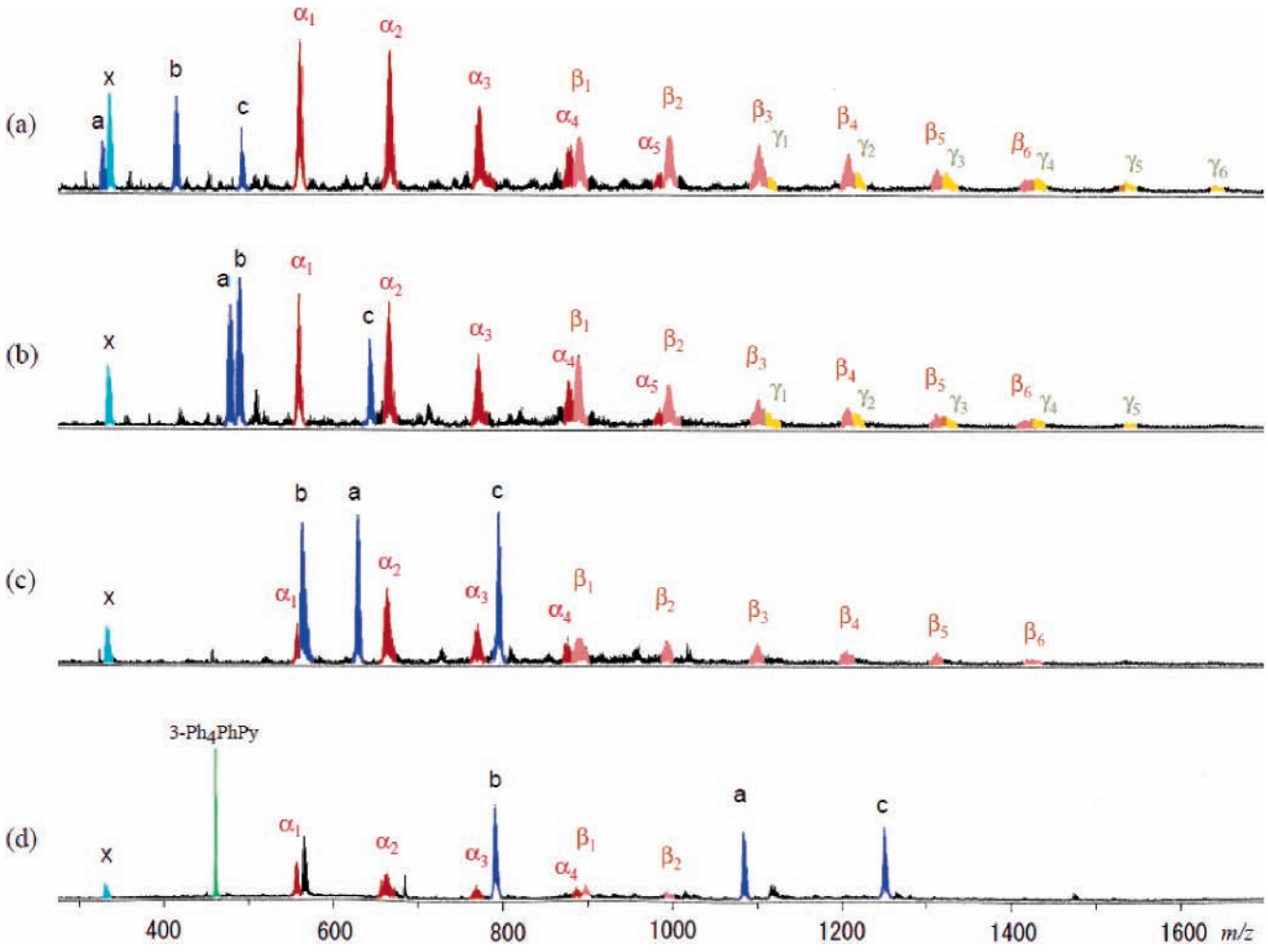


Figure 1. MALDI TOF mass spectra of (a) $Pd(OAc)_2(Py)_2$, (b) $Pd(OAc)_2(3\text{-PhPy})_2$, (c) $Pd(OAc)_2(3,5\text{-}Ph_2Py)_2$, and (d) $Pd(OAc)_2(3\text{-}Ph_4\text{-}PhPy)_2$ with dithranol as the matrix. X: Pd(dithranol).

Table 1. Characteristic Mass (*m*/*z*) in Figure 1

mark	formula or equation	*m*/*z* L in $Pd(OAc)_2(L)_2$ Py	3-PhPy	3,5-Ph_2Py	3-Ph_4PhPy
a	$Pd(OAc)(L)_2$	323	475	627	1084
b	$Pd_2(OAc)_2(L)$	410	486	562	790
c	$Pd_2(OAc)_2(L)_2$	488	640	792	1250
α_x[a]	$Pd_{(x+4)} + 27$	557, 663, 769, 875, 981			
β_y[b]	$Pd_{(y+7)} + 38$	886, 992, 1098, 1204, 1310, 1416			
γ_z[c]	$Pd_{(z+9)} + 50$	1110, 1216, 1322, 1428, 1534, 1640			

[a] $x = 1-5$. [b] $y = 1-6$. [c] $z = 1-6$.

but all accord with the calculated values according to the formulas (Table 1). In contrast, a series of peaks α_x, β_y, and γ_z appeared at the same positions throughout in Figure 1a−d without regard to L having the constant peak interval of 106, the atomic weight of Pd. Therefore, the peaks α_x, β_y, and γ_z must be due to three different kinds of Pd oligomers (degree of the oligomerization: $\gamma_z > \beta_y > \alpha_x$) which do not contain the pyridine ligands (L). Each peak position of α_x is given by the equation $Pd_{(x+4)} + 27$, β_y is given by $Pd_{(y+7)} + 38$, and γ_z is given by $Pd_{(z+9)} + 50$ (x, y, z = 1, 2, 3, ...), respectively. Although accurate structures and compositions of the oligomers are not obvious, the α_x series might be assigned to $Pd_{(x+2)}(OAc)_4(H)_3$, β_y to $Pd_{(y+5)}(OAc)_4(C)(H)_2$, and γ_z to $Pd_{(z+7)}(OAc)_4(C)_2(H)_2$ (x, y, z = 1, 2, 3, ...).

It is worth noting that the degree of oligomerization is affected by the nature of the pyridine ligand (L). Though an absolute intensity of each mass peak cannot be compared, relative intensities of the groups $\Sigma(a + b + c)$, $\Sigma\alpha_x$, $\Sigma\beta_y$, and $\Sigma\gamma_z$ (Σ indicates a total intensity of each group) were shown in Figure 2: in each mass spectrum the entire intensity ($\Sigma(a + b + c) + \Sigma\alpha_x + \Sigma\beta_y + \Sigma\gamma_z$) is normalized to 100%. Figures 1 and 2 indicate that the 3-Ph_4PhPy ligand (Figure 1d and Figure 2d) successfully suppresses higher oligomerization of the palladium center, while Py, 3-PhPy, and 3,5-Ph_2Py ligands afford a considerable amount of the Pd oligomers. This ligand effect is similar to one observed in the air oxidation of alcohols catalyzed by these complexes.[4] In the catalytic reactions, $Pd(OAc)_2$(3-Ph_4PhPy)$_2$ did not

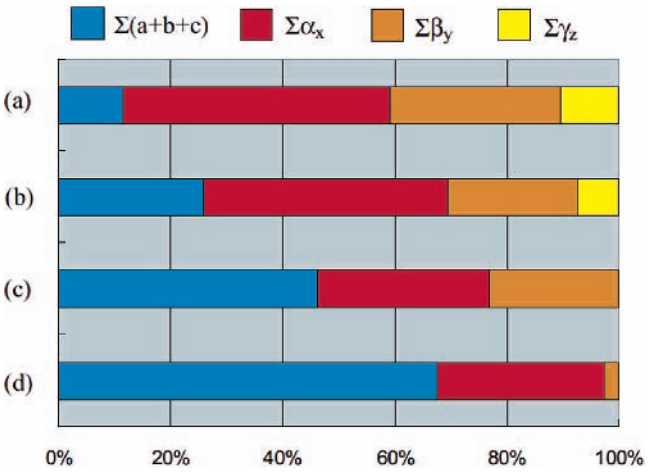


Figure 2. Relative peak intensities of the MALDI TOF mass spectra in Figure 1: (a) $Pd(OAc)_2(Py)_2$, (b) $Pd(OAc)_2$(3-PhPy)$_2$, (c) $Pd(OAc)_2$(3,5-Ph_2Py)$_2$, (d) $Pd(OAc)_2$(3-Ph_4PhPy)$_2$.

afford the Pd black and kept the catalytic activity to afford products in high yields, while $Pd(OAc)_2(Py)_2$, $Pd(OAc)_2$(3-PhPy)$_2$, and $Pd(OAc)_2$(3,5-Ph_2Py)$_2$ as the catalyst provided the Pd black, and gave the corresponding ketones only in low yields.

The rigid Ph_4PhPy moiety spatially spreads out and covers the wide area, as the X-ray crystal structure of $Pd(OAc)_2$-(3-Ph_4PhPy)$_2$[4] suggested. Such a rigid and widely spread substituent on the pyridine ligand will keep the Pd center apart and prevent Pd oligomerization (aggregation).

In conclusion, we found that the MALDI TOF mass with dithranol as the matrix is particularly a successful approach to examine the Pd oligomerization. The degree of oligomerization is influenced by the pyridine ligands (L), and this ligand effect is similar to one observed for Pd black formation in air oxidation of alcohols. Noteworthily, once the oligomerization occurs, all the resulting oligomers (α_x, β_y, and γ_z) no longer contain the pyridine ligands (L).

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