# Synthesis of 1-Nonene from Decanoic Acid by Polymer-Bound Palladium Complexes

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(Received September 5, 1997; CL-970683)

$(PhCN)_2PdCl_2$ or $Pd(OAc)_2$ was immobilized on polyorganosiloxane bearing phosphine group as the support. The catalytic activity of polymer-bound palladium complex revealed higher activity and selectivity than the homogeneous catalyst for the synthesis of 1-nonene from decanoic acid.

In recent years extensive studies have been revealed on homogeneous catalysts heterogenized by attachment to insoluble polymer supports. The fixed position of the catalyst on the polymer may impart great site isolation and, in some cases, this can drastically influences the catalytic behavior.[1-5] These catalysts offer its easy recovery and possible re-use without serious loss of activity, and the enhancement of its selectivity and activity in comparison with those exhibited by the conventional homogeneous catalysts.

Olefins are the important materials of many organic compounds in the chemical industry. Although today these are manufactured by ethylene oligomerization processes, the selective production of olefins via decarbonylation/dehydration of the corresponding carboxylic acid may be viewed as one possible method from renewable resources. The decarbonylation/dehydration of aliphatic carboxylic acid to olefins was first reported by Prince et al.[6] Foglia et al[7] reported the decarbonylation/dehydration of stearic acid to heptadecene catalyzed over rhodium complex catalysts. Recently Miller and Zahang[8,9] studied the synthesis of 1-nonene from decanoic acid with Pd or Rh-based soluble catalyst, but very few reports have been published on the reaction with polymer-bounded metal complexes.

This research was intended to study the activity and selectivity of polymer supported palladium complexes on the decarbonylation/dehydration of decanoic acid to 1-nonene shown in eqn.(1).

$$C_9H_{19}CO_2H + Ac_2O \rightarrow C_9H_{18} + CO + 2AcOH \qquad (1)$$

Polyorganosiloxane(POS) was obtained by the reaction of $(C_6H_6)_2PC_2H_4Si(OCH_3)_3$ and $Si(OCH_3)_4$ in a nitrogen atmosphere for 2 h. POS was collected by filtration, washed with water and acetone, and dried in vacuum at room temperature. POS-bound palladium complexes were prepared as follows, POS support and the desired amount of $(PhCN)_2PdCl_2$ or $Pd(OAc)_2$ were slurried in acetone. After being refluxed for 5 h, the slurry was filtered, washed with acetone, and dried in vacuum at room temperature.

Catalytic reactions were carried out in a round-bottomed flask fitted with a distillation head at atmospheric pressure. The flask was charged with Pd catalyst, the desired amount of phosphine ligand and the equimolar mixture of decanoic acid and acetic anhydride. Temperature was raised to 250°C with vigorous stirring. During the reaction, the initial level of the reactor contents was maintained by continuously introducing a feed mixture. In order to determine the product composition, the distillate product was sampled after the stop of the reaction and analyzed on a cappillary gas chromatograph . The gas chromatographanalyses of the distillate showed the presence of 1-nonene. No nonane was detected in the reaction and the byproducts in the distillate product were trace amounts of trans- and cis-2-nonene.

Figure 1 shows the relationship between the catalyst turnover number (TON: moles of olefin product formed per mole of catalyst used) and the additional $PPh_3$ for the synthesis of 1-nonene from decanoic acid by POS-supported $PdCl_2$ and unsupported $PdCl_2$ catalysts, when the molar ratio of the added $PPh_3$ to Pd catalyst was changed from 20 to 100. In the absence of $PPh_3$, the system exhibited little catalytic activity. As for the POS-supported Pd catalyst with 4 of P/Pd which indicates the mole ratio of the phosphine group on POS to Pd, the TON increased gradually with the addition of $PPh_3$ ligand. This means that the presence of $PPh_3$ ligand is very important to achieve high catalyst efficiency for this reaction. As for POS-supported Pd catalyst with 32 of P/Pd, there appeared the maximum value of the additional $PPh_3$ content in the activity. This feature suggests that the presence of excess $PPh_3$ in the reaction medium showed the retarding effect in the catalytic activity. TON for unsupported Pd catalyst exhibited a similar behavior. In comparison with TON for these catalysts, the TON for supported-$PdCl_2$ catalyst with 32 of P/Pd was apparently higher than that for unsupported Pd catalyst.

In order to explore the influence of P/Pd ratio in supported catalyst, the reaction was carried out by varying the molar ratio of P/Pd of supported Pd catalysts under the condition of 50 of $PPh_3$/Pd. As can be seen in Figure 2, the TON depends largely on the ratio of P/Pd in the catalyst. The TON increased gradually with increasing the ratio of P/Pd to 32, while it showed a slight

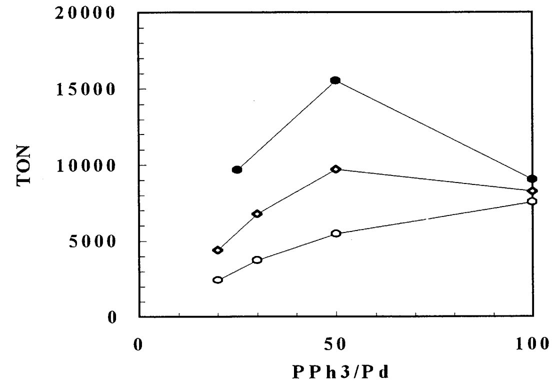

**Figure 1.** Comparison of TON catalyzed over unsupported catalyst with that catalyzed over supported catalysts. Reaction condition: 250°C, [$C_9H_{19}CO_2H$]/ [$Ac_2O$]= 1 mol / mol, [Pd Catalyst]=0.01mol% based on the initial charge of decanoic acid, Supported catalyst: ( ○ ) P/Pd=4, ( ● ) P/Pd=32, (◇)unsupported catalyst.

decrease above 32 of P/Pd. In comparison with TON of 10000 for the unsupported catalyst, the TON for the supported catalysts above 25 of P/Pd ratio showed a higher value than that for the unsupported catalyst. In general, activity of supported catalyst is lower than that of homogeneous catalyst owing to intraparticle substrate transport limitations.[3,10] One of reasons for high TON can be considered that the phosphine group on POS support may coodinate to Pd metal to form other kinds of active sites.[11] The other reason may be explained by the fact that Pd compounds are well dispersed on the surface of the support and thus the effective surface of Pd is increased on the support. In the case of the supported Pd catalysts below 25 of P/Pd ratio, its TON was lower than that for the unsupported catalyst. This may be due to a decrease in the dispersion of Pd compounds for the supported catalyst with lower P/Pd ratio, which has high content of Pd. As a consequence, it appears lower active than the supported catalyst above 25 of P/Pd ratio even though the catalytically active species may be the same.

The selectivity toward 1-nonene transformation in all the experiments were showed in Figure 3. On increasing the $PPh_3$/Pd ratio, the change in the selectivity was very small for the supported and unsupported catalysts. In other words, the selectivity is independent of the molar ratio of P/Pd of POS-supported catalysts and it should be emphasized that the selectivity was apparently higher than that for the unsupported catalyst. The difference in the selectivity for these catalysts may be related to the ligands of the homogeneous complex and the POS-supported catalyst. It has been reported that the kind of ligand has a great influence on the selectivity for the decarbonylation/dehydration of carboxylic acid. According to Miller et al.[8] the ligand $PMe_2Ph$ with the homogeneous Rh-based catalyst provides a higher selectivity than that using phosphine ligand as $PPh_3$ or $P(C_6H_{11})_2$ Ph. Based on these results, they indicated that efficient removal of the olefin product from the reaction system is important to obtain a high degree of olefin selectivity. This means that it is necessary to remove the produced olefin from the active site of catalyst in order to increase the selectivity to $\alpha$-olefin. Therefore, upon applying this discussion to the reason for the high selectivity on the supported Pd catalyst, olefin produced on the Pd active site easily desorbs from the catalyst surface, resulting in a higher selectivity than that for the homogeneous catalyst. The electronic effect of the polymer support may play a significant role for the desorption of produced olefin. The characteristic behavior of the selectivity for the supported catalyst was also obtained by using $PCy_3$ ligand as in the case with $PPh_3$. On increasing the $PCy_3$/Pd molar ratio, the selectivity for the supported catalyst gradually decreased from 96% to 85%, while that for the unsupported catalyst changed from 92% to 81%. Even in the case of $PCy_3$ ligand it must be noted that the selectivity for the supported catalysts was apparently higher than that for the unsupported catalyst. With respect to TON, however, the observed values with $PPh_3$, which are higher than those with $PCy_3$, suggest that $PPh_3$ ligand is favorable for this reaction.

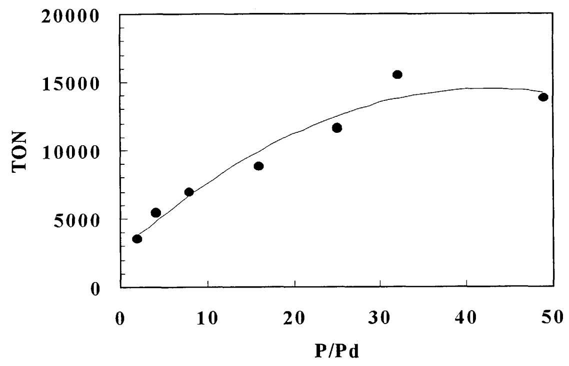

**Figure 2.** TON over supported catalysts as a function of P/Pd molar ratio under $PPh_3$/Pd=50. Reaction conditions are the same as in Figure 1.

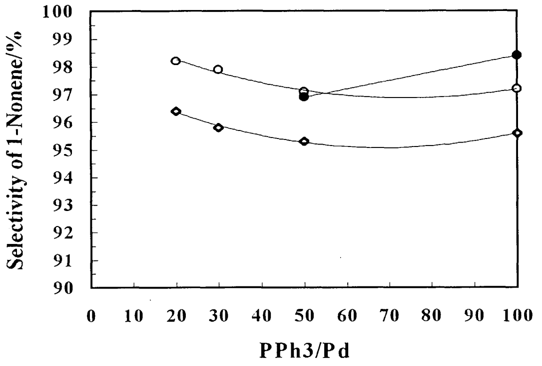

**Figure 3.** Relationship between the selectivity to 1-nonene and added $Ph_3P$ over supported catalysts and unsupported catalyst. Supported catalyst: ( ○ ) P/Pd=4, ( ● ) P/Pd=32, ( ◇ ) unsupported catalyst.

Although from the viewpoint of industrial utilization it is necessary to do the more detailed investigations, we will examine the effect of the various kinds of support and ligand for the decarbonylation/dehydration of aliphatic carboxylic acid to olefins in the next paper.

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