

# MODIFICATION OF PALLADIUM METALLIC CATALYST WITH POLYMER-ANCHORED THIOETHER LIGANDS

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## ABSTRACT

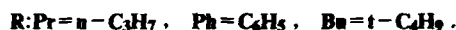
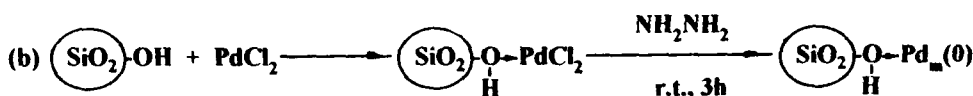
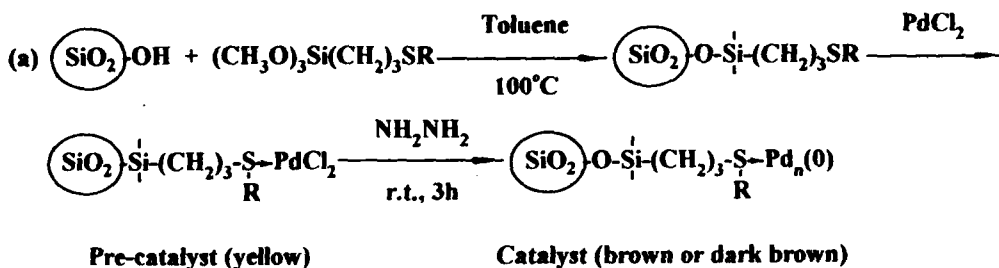
A well-dispersed metallic palladium catalyst modified by polymer-anchored thioether ligands was used for the hydrogenation of cyclopentadiene to cyclopentene with high activity and selectivity in ambient condition. The evidences to show the modification of catalytic properties by polymer anchored ligands were given.

The catalytic properties of metallic catalysts can be manipulated by the addition of ligands which are known as promoters or modifiers. Boitiaux et al.<sup>[1]</sup> reported that the presence of piperidine increased the hydrogenation rates of unsaturated hydrocarbons and the selectivity for the formation of olefins catalysed by palladium. Nishimura and co-workers<sup>[2]</sup> used phenylacetaldehyde as a modifier to improve the selectivity of palladium catalyst for the hydrogenation of nonconjugated dienes to monoenes. Another famous example was the modified Raney nickel catalyst<sup>[3]</sup>, in which Raney nickel was modified with an optically active amino acid or hydroxy acid and was endowed with the new function of asymmetric hydrogenation. Apparently, the addition of the soluble additive will contaminate the products or in some cases lead to the additional metal leaching caused by coordination.

Recently, in a study of catalytic hydrogenation by making a comparison between the results found from palladium on metal oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2\text{-MgO}$ ) bearing phosphine ligands and Pd/C catalyst, Augustine et al.<sup>[4]</sup> proposed that the pendent phosphines interacted with the palladium metal supported on modified oxides and thus influenced the catalytic properties, but no further evidence was given.

In this communication, direct evidences to show the modification of catalytic properties by polymer anchored ligands were presented. The palladium catalysts modified by anchored thioether ligands were synthesized based on the unique affinity for sulphur to platinum metals<sup>[5]</sup>. This kind of catalysts showed high catalytic activity and selectivity for the selective hydrogenation of cyclopentadiene (CPD) to cyclopentene (CPE).

The catalysts were prepared according to Scheme 1. For the purpose of comparison, the catalyst Pd/ $\text{SiO}_2$  was similarly prepared without using coupling ligands.



Scheme 1 Route for the preparation of the palladium catalysts.

a) For thioether-containing palladium catalyst

b) For palladium on neat silica as a counterpart

The results of catalytic hydrogenation of CPD were listed in Table 1.

Table 1 The results of catalytic hydrogenation of cyclopentadiene<sup>a</sup>

| Catalyst                        | Cat-SPr-Pd |      |      |      |      |                   | Cat-SBu-Pd |      |      |      |      |      | Cat-SPh-Pd |      |      |      |  |  | Pd/<br>SiO <sub>2</sub> <sup>b</sup> |
|---------------------------------|------------|------|------|------|------|-------------------|------------|------|------|------|------|------|------------|------|------|------|--|--|--------------------------------------|
|                                 | 1          | 2    | 4    | 6    | 8    | 12                | 1          | 2    | 4    | 6    | 8    | 1    | 2          | 4    | 6    | 8    |  |  |                                      |
| S<br>(mmol/g)                   | 0.825      |      |      |      |      |                   | 0.568      |      |      |      |      |      | 0.565      |      |      |      |  |  | —                                    |
| S/Pd                            | 1.3        | 2.0  | 4.0  | 5.6  | 8.2  | 12.0              | 1.5        | 2.0  | 3.9  | 6.0  | 7.9  | 1.4  | 2.0        | 3.7  | 5.8  | 8.0  |  |  | —                                    |
| Pd (%)                          | 6.7        | 4.3  | 2.1  | 1.5  | 1.1  | 0.73              | 4.0        | 3.0  | 1.6  | 1.0  | 0.76 | 4.3  | 3.0        | 1.6  | 1.0  | 0.76 |  |  | 1.2                                  |
| V <sub>1</sub> <sup>c</sup>     | 1.77       | 1.71 | 1.71 | 1.82 | 1.35 | 0.59              | 1.96       | 3.53 | 3.03 | 2.58 | 2.47 | 1.80 | 2.50       | 2.45 | 2.76 | 0.50 |  |  | 4.20                                 |
| V <sub>2</sub> <sup>d</sup>     | 1.00       | 1.10 | 1.11 | 0.51 | 0.35 | 0.13              | 0.72       | 1.72 | 1.21 | 0.88 | 0.74 | 1.06 | 1.86       | 1.44 | 1.16 | 0.16 |  |  | 1.96                                 |
| Selectivity <sup>e</sup><br>(%) | 94.9       | 97.7 | 97.0 | 75.8 | 75.9 | 73.0 <sup>f</sup> | 95.3       | 98.0 | 94.3 | 92.8 | 90.0 | 96.1 | 97.0       | 94.9 | 93.8 | 86.9 |  |  | 82.8                                 |

a) Reaction condition: Pd, 0.06 mmol; CPD, 0.50 mL; Solvent: methanol, 19.50 mL; T: 30.0 °C; P<sub>H<sub>2</sub></sub>: 1.01·10<sup>5</sup> Pa; Activation time: 1h.

b) Pd/SiO<sub>2</sub> was prepared as in Scheme 1.

c) The initial rate of hydrogenation for CPD (10<sup>-1</sup> mol H<sub>2</sub>·g-atom Pd<sup>-1</sup>·s<sup>-1</sup>).

d) The average rate of hydrogenation for CPE (the same unit as above).

e) The selectivity to CPE at the 100% conversion of CPD.

f) The selectivity to CPE at 96.3% conversion of CPD.

It could be deduced from these data that (1) The modification of metallic palladium catalysts by polymer anchored thioether ligands improved the selectivity for CPE formation from 83% to 98% with slight decrease in the initial hydrogenation rate of CPD from 4.2 to 3.5 (10<sup>-1</sup>mol H<sub>2</sub>·g-atom Pd<sup>-1</sup>·s<sup>-1</sup>). (2) The effect of thioether ligands on catalytic properties was dependent on their

relative amounts in the catalyst (as the molar ratio of ligand to palladium in a complex). That the active species of the catalyst were the well-dispersed metallic palladium particles rather than the palladium (0) or (II) complexes was confirmed by mercury poison experiment, XPS data and transmission electron microscopy (TEM). First, the pre-catalyst was inactive, in which palladium was verified to be in +2 valency (cf. XPS data from Table 2).

Table 2 XPS data for the catalysts and relevant compounds

| Compound                     | Binding Energy <sup>a)</sup> (eV) |                 |
|------------------------------|-----------------------------------|-----------------|
|                              | Pd <sub>3d 5/2</sub>              | S <sub>2p</sub> |
| Sup-SPr                      | -----                             | 163.9           |
| Pre-SPr-PdCl <sub>2</sub> -2 | 337.8                             | 163.8           |
| Cat-SPr-Pd-1                 | 335.3                             | 163.9           |
| Cat-SPr-Pd-2                 | 335.2                             | 163.9           |
| Cat-SBu-Pd-2                 | 335.4                             | 163.9           |
| Pd (metal)                   | 335.5                             | -----           |
| Pd/SiO <sub>2</sub> (1.2%)   | 335.4                             | -----           |
| PdCl <sub>2</sub>            | 338.1 <sup>b)</sup>               | -----           |

a) The binding energy values are referred to C<sub>1s</sub> (285.0 eV)

b) From Ref.6.

Mercury poison experiments<sup>[7]</sup> which distinguished heterogeneous and homogeneous processes were conducted by stirring an active catalyst with mercury for 20 minutes in a hydrogenation reaction apparatus. After that, in no instance was any catalytic activity observed. It was concluded that the hydrogenation was catalysed heterogeneously by finely divided palladium metal phase rather than homogeneously palladium (0) complexes. TEM showed that the particle sizes of palladium metal in modified catalyst (Cat-SPr-Pd-2) were distributed in narrow ranges from 1 to 6 nm, mainly from 2 to 4 nm. On the other hand, particle sizes for catalyst Pd/SiO<sub>2</sub> were much larger and with a broader distribution (Figure 1).

The results showed that the anchored thioether ligands could prevent the palladium metal particles from aggregation. This ligand effect was in concordance with the statement in literature [8].

The curves for consumption of CPD and the evolution of products as a function of time are plotted in Figure 2. The hydrogenation of CPD catalysed by the modified catalyst (Cat-SBu-Pd-2) is very selective for CPE formation. In Figure 2 (a) it is observed that the rate of CPE consumption is strongly inhibited, that

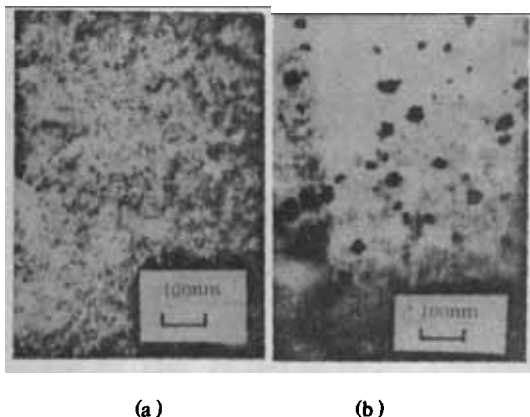


Fig.1 The electron micrographs of the catalysts.

a) Cat-SPr-Pd-2;

b) Pd/SiO<sub>2</sub> (1.2%).

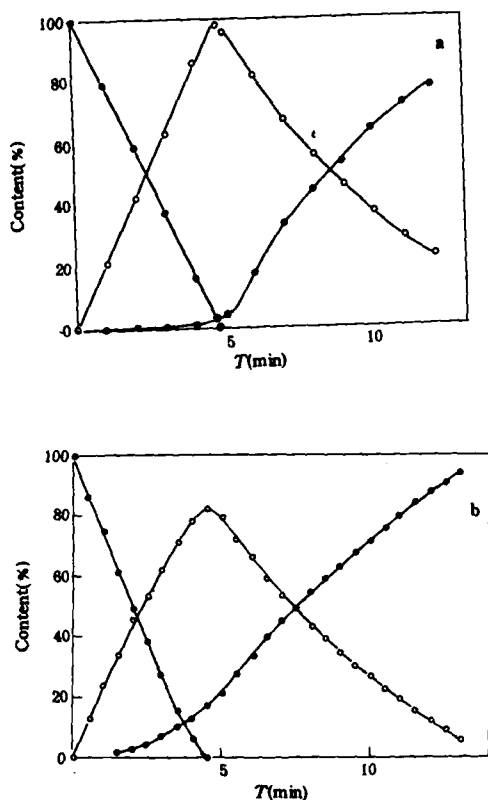


Figure 2 CPD consumption and evolution of different products over palladium catalysts

a) Cat-SBu-Pd-2

b) Pd/SiO<sub>2</sub>

● CPD; ○ CPE; ● CPA.

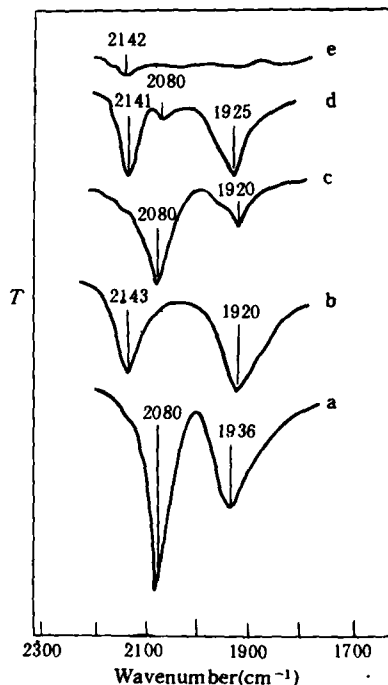


Fig.3 IR spectra of CO adsorption probe on catalysts

a) Pd/SiO<sub>2</sub> (1.2%); b) Cat-SPr-Pd-2;

c) Cat-SPh-Ph-2; d) Cat-SBu-Pd-2;

e) Cat-SBu-Pd-6.

Experimental conditions:

The wafer was made from catalysts in  $3.5 \text{ mg} \cdot \text{cm}^{-2}$ , it was treated in hydrogen ( $5.33 \cdot 10^4 \text{ Pa}$ ) for 12 h at 498 K, evacuated for 1 h to  $2.67 \cdot 10^{-3} \text{ Pa}$ ; and then cooled to 293 K under dynamic vacuum. The base-line spectrum was recorded under vacuum and then the wafer was equilibrated with  $4.00 \cdot 10^4 \text{ Pa}$  of CO for 20 min., spectra were then recorded.

is, very little cyclopentane (CPA) is formed from the beginning of the reaction, while the catalyst Pd/SiO<sub>2</sub> — palladium on neat silica without thioether groups — exhibits a poor selectivity.

The effect of anchored thioether ligands also reflects on the IR spectra of CO absorption over palladium (Figure 3).

Frequency shift and decrease in absorbance of CO absorption bands were believed to be due to both the long range electronic interaction and block adsorption sites on palladium surface by sulphur-containing ligands<sup>[11,9]</sup>. Further study on the effect of different ligands on palladium catalyst is in progress.

**Keywords :**

Modified palladium catalyst; Selective hydrogenation; Thioether ligands; Cyclopentadiene

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