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HYDROGENATION OF ALDEHYDES AND KETONES CATALYZED BY PALLADIUM COMPLEXES OF SILICA-SUPPORTED POLY-γ-CYANOPROPYLSILOXANE AND POLY-γ-AMINOPROPYLSILOXANE

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Summary

Pd complexes of silica-supported poly-γ-cyanopropylsiloxane and poly-γ-aminopropylsiloxane have been found to catalyze the heterogeneous hydrogenation of aldehydes and ketones at room temperature under an atmospheric pressure of hydrogen. The catalytic activities of these two complexes are similar and are greatly affected by N/Pd atomic ratio in the complexes. These complexes are stable and can be reused.

Introduction

It has been found that many complexes of transition metals are catalysts for the homogeneous hydrogenation of carbon–carbon multiple bonds under ambient conditions [1]. However, the hydrogenation of aldehydes and ketones catalyzed by transition metal complexes usually requires rather drastic conditions, i.e., high temperature and high hydrogen pressures [2–4]. Moreover, it is difficult to recover them from the reaction products. In order to overcome this problem, a polymer-supported metal complex, a rhodium complex of polystyrene with anthranilic acid groups, was examined as the hydrogenation catalyst of aldehydes and ketones. However, the catalytic activity is very low and it also requires as reaction conditions high temperature (100°C) and high pressure (800–1000 psig) [5].

In our previous works [6,7], we reported that Pd complexes of silica-supported poly-γ-cyanopropylsiloxane (abbreviated as $\textcircled{Si}$–CN–Pd) and poly-γ-aminopropylsiloxane ($\textcircled{Si}$–NH_2–Pd) could be used as the hydrogenation catalysts for olefins. Recently, we have found that these two polymer-supported Pd complexes are also effective catalysts for hydrogenation of aldehydes and ketones at room temperature and atmospheric pressure. In this paper we wish to report the detailed experimental results.

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Experimental

A. Preparation of silica-supported poly-γ-cyanopropylsiloxane

Toluene (200 ml), 10 g of γ-cyanopropyltriethoxysilane and 10 g of fumed silica (surface area, 370 m^2/g) were placed in a flask equipped with a stirrer, a dropping funnel and a reflux condenser. After stirring for 10 min, 12 ml of ethanol solution containing 4 ml of water and 0.2 ml of 10% hydrochloric acid was added dropwise, and the mixture was heated to reflux. During the reflux the white mixture became transparent. After 1 h reflux, toluene and ethanol were distilled off in vacuo. The nitrogen content of the product was 4.0% (determined by elemental analysis).

B. Preparation of silica-supported poly-γ-aminopropylsiloxane

The method was similar to A [7]. However, 10 g of γ-aminopropyltriethoxysilane was used instead of 10 g of γ-cyanopropyltriethoxysilane, and hydrochloric acid was not added. The nitrogen content of the product was 3.6 wt% (determined by elemental analysis).

C. Preparation of silica-supported poly-γ-cyanopropylsiloxane-Pd complex (Ⓢⓘ-CN-Pd)

Several silica-supported poly-γ-cyanopropylsiloxane-Pd complexes with different N/Pd atomic ratios were prepared. For example, 0.06 g (0.28 mmol) of $PdCl_2 \cdot 2H_2O$, 0.75 g (2.14 mg atom N) of silica-supported poly-γ-cyanopropylsiloxane(N wt%: 4) and 20 ml of ethanol were placed in a three-necked flask (50 ml) equipped with a stirrer, a reflux condenser and a gas inlet tube. The mixture was stirred and refluxed under nitrogen for 6 h. The white solid particles became grey and the dark brown solution turned colorless and transparent. The product was filtered, and dried in air, and then in vacuo. The N/Pd atomic ratio of the product was 7.6 (calculated from the amounts of silica-supported poly-γ-cyanopropylsiloxane and $PdCl_2 \cdot 2H_2O$ used). The infrared spectrum showed that the product was a Pd complex (*trans*-Pd-chloride stretching appeared at 351 cm^{-1} [8]).

D. Preparation of silica-supported poly-γ-aminopropylsiloxane-Pd complex (Ⓢⓘ-NH_2-Pd)

The method was similar to C [7]. However, 0.033 g (0.84 mg atom N) of silica-supported poly-γ-aminopropylsiloxane (N wt%: 3.6) was used. The N/Pd atomic ratio of the product was 3.0.

E. Hydrogenation of aldehydes and ketones

The Pd complex (0.075 mmol Pd), solvent (10 ml) and substrate (0.05 mol or 0.01 mol) were placed in a glass reactor with a gas inlet tube, a gas outlet tube and a jacket. The reactor was fixed on a shaker and connected to a gas burette and a hydrogen storage bottle. Constant temperature water was passed through the jacket from a water bath. The system was alternately evacuated and flushed with hydrogen five times, and hydrogen pressure was set near 1 atm. The mixture was shaken and then the volume of hydrogen uptake was measured. The reaction products were analysed by GLC.

TABLE 1

HYDROGENATION RATES OF ALDEHYDES AND KETONES WITH (Si)-CN-Pd AND (Si)-NH_2-Pd[a]

Substrate	Initial rate (ml/min)	
	(Si)-CN-Pd	(Si)-NH_2-Pd
Benzaldehyde	8.0	7.5
p-Hydroxybenzaldehyde	6.7	6.1
o-Hydroxybenzaldehyde	8.0	4.2
p-Dimethylaminobenzaldehyde	11.2	6.0
o-Chlorobenzaldehyde	3.1	4.6
n-Hexanal	2.5	3.3
Propanal	4.0	6.1
Acetophenone	9.0	8.4
Benzophenone	3.5	3.1
Cyclohexane-1,3-dione	6.0	12.0
Cyclohexanone	1.0	1.0
Acetylacetone	1.5	1.0
Acetone	0.86	1.1

[a] Complex: Pd, 0.075 mg atom; N/Pd atomic ratio, (Si)-CN-Pd 7.6, (Si)-NH_2-Pd 3.0; substrate, 0.05 mmol; solvent EtOH(10 ml); 30°C, 1 atm.

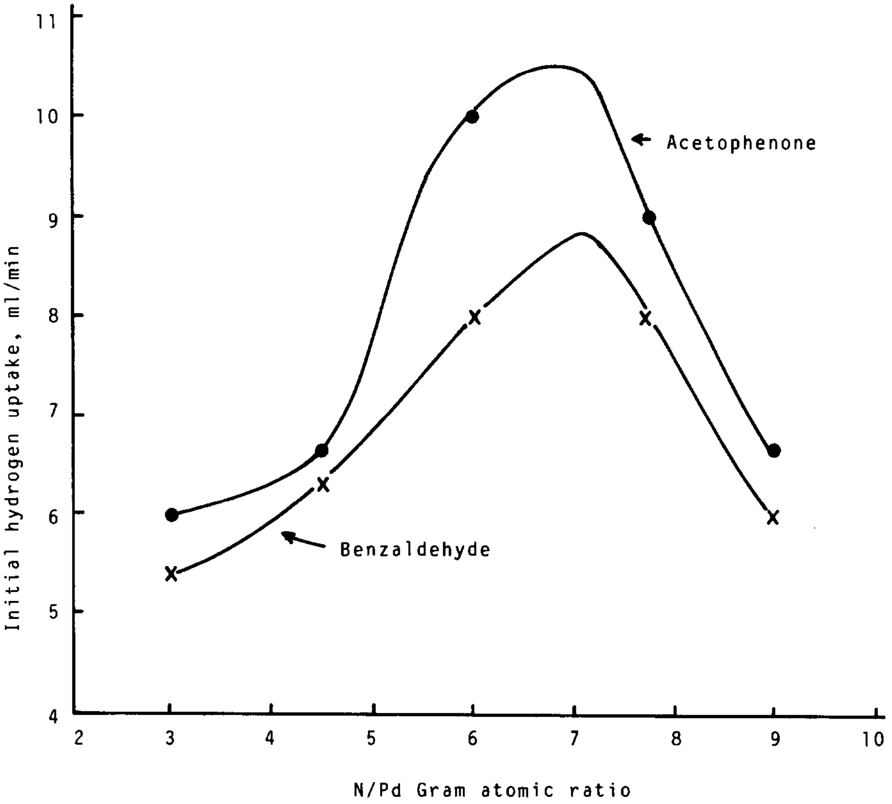

Fig. 1. The Relationship between the rate of hydrogenation and N/Pd atomic ratio in (Si)-CN-Pd. Complex: Pd. 0.075 mg atom; solvent, EtOH (10 ml); Substrate, 0.05 mol; 30°C, 1 atm.

Results and discussion

Various aldehydes and ketones were hydrogenated by using Ⓢi–CN–Pd and Ⓢi–NH_2–Pd. The results are shown in Table 1. As can be seen, the catalytic activities of these two complexes for hydrogenation of aldehydes and ketones are similar. They have relatively high catalylic activities for hydrogenation of aromatic aldehydes (e.g. benzaldehyde, *p*-hydroxybenzaldehyde, *o*-hydroxybenzaldehyde, *p*-dimethylaminobenzaldehyde and *o*-chlorobenzaldehyde), aliphatic aldehydes (e.g. n-hexanal and propanal) and aromatic ketones (e.g. acetophenone and benzophenone). However, their catalytic activities are relatively low for hydrogenation of aliphatic ketones (e.g. cyclohexanone, acetylacetone and acetone) except cyclo-hexane-1,3-dione.

The hydrogenations of benzaldehyde and acetopheone were studied in detail.

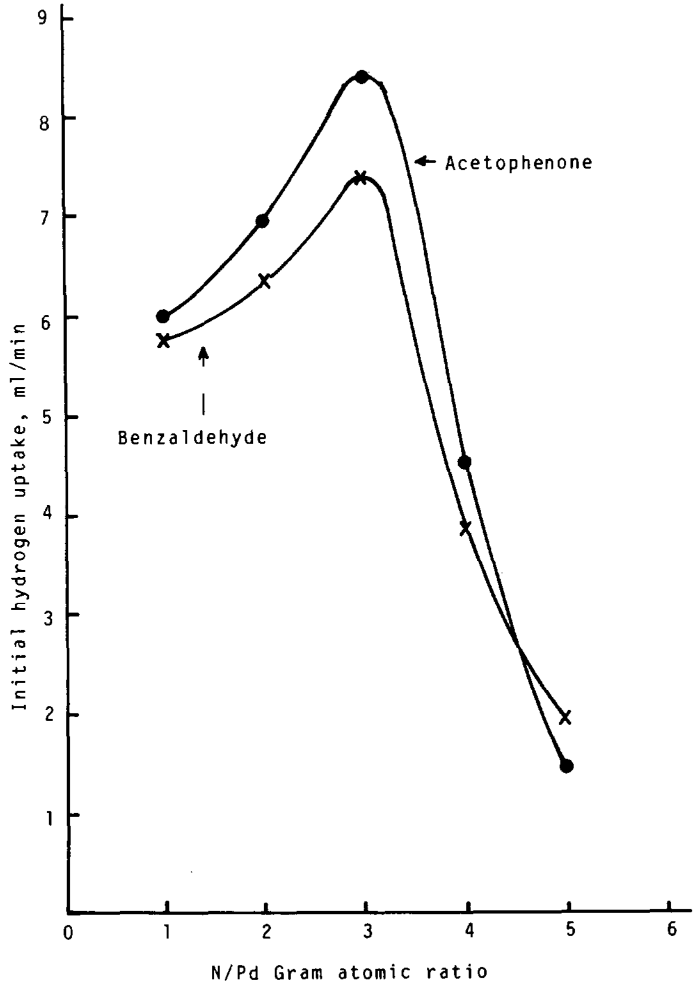

Fig. 2. The Relationship between the rate of hydrogenation and N/Pd atomic ratio in Ⓢi–NH_2–Pd. Complex: Pd. 0.075 mg atom: substrate, 0.05 mol; solvent, EtOH (10 ml): 30°C, 1 atm.

TABLE 2

EFFECT OF SOLVENT ON BENZALDEHYDE AND ACETOPHENONE HYDROGENATION [a]

Catalyst	Solvent	Initial rate (ml/min)	
		Benzaldehyde	Acetophenone
(Si)–CN–Pd	Ethanol	8.0	9.0
	i-Propanol	9.6	9.2
	THF	7.5	6.7
	Hexane	8.6	3.3
	Toluene	5.0	1.0
(Si)–NH_2–Pd	Ethanol	7.5	8.4
	i-Propanol	7.6	5.5
	THF	4.0	2.0
	Hexane	6.6	3.6
	Toluene	3.8	0.8

[a] Complex: Pd, 0.075 mg atom, N/Pd atomic ratio, (Si)–CN–Pd 7.6, (Si)–NH_2–Pd 3.0; substrate, 0.05 mmol; solvent, 10 ml; 30°C, 1 atm.

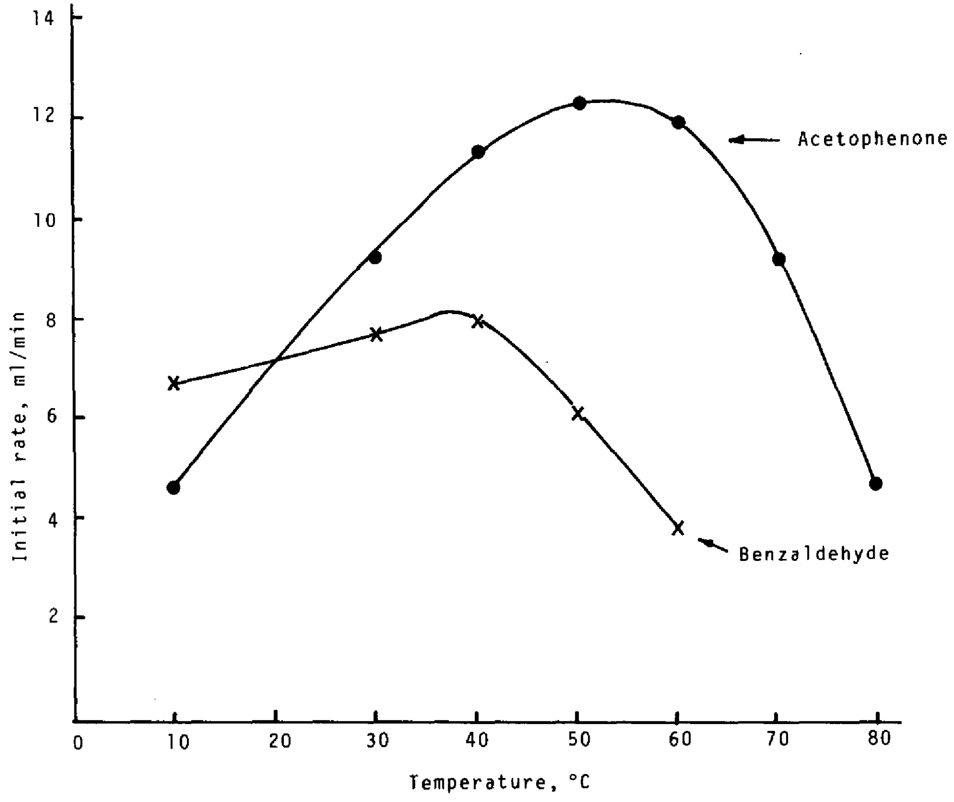

Fig. 3. Influence of temperature on the rate of hydrogenation catalysed by (Si)–CN–Pd. Complex: Pd, 0.075 mg atom; N/Pd, 7.6; substrate, 0.05 mol; solvent, EtOH (10 ml); 1 atm.

TABLE 3

THE STABILITIES OF THE CATALYSTS IN THE RECYCLING PROCESSES

Catalyst	Substrate	Time for complete hydrogenation[a] (min)		
		1	2	3
(Si)-CN-Pd	Benzaldehyde	26	28	30
	Acetophenone	26	33	47
(Si)-NH$_2$-Pd	Benzaldehyde	38	39	43
	Acetophenone	39	42	44

[a] Conversion, 100%; 1, with fresh catalyst; 2, with once-used catalyst; 3, with twice-used catalyst; complex: Pd, 0.075 mg atom, N/Pd, (Si)-CN-Pd, 7.6, (Si)-NH$_2$P-Pd, 3.0; substrate, 0.01 mol; solvent, EtOH (10 ml); 30°C, 1 atm.

Figures 1 and 2 show the relationship between the rate of hydrogenation and N/Pd atomic ratio in the complex. When (Si)-CN-Pd was used, whether the substrate is benzaldehyde or acetophenone, the active peak appears at about 7 N/Pd atomic ratio. When (Si)-NH$_2$-Pd is used, the active peak appears at an N/Pd atomic ratio

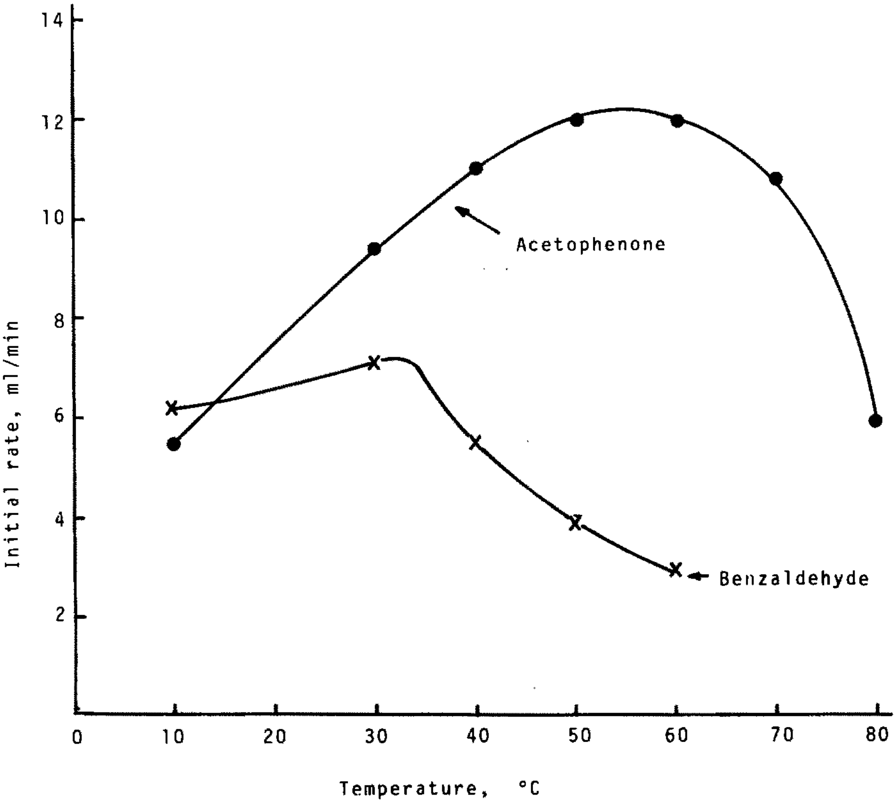

Fig. 4. Influence of temperature on the rate of hydrogenation catalyzed by (Si)-NH$_2$-Pd. Complex: Pd, 0.075 mg atom; N/Pd, 3.0; Substrate 0.05 mol; solvent, EtOH (10 ml); 1 atm.

of about 3. These phenomena are similar to those found in the hydrogenation of olefins by these two catalysts [6,7].

The effect of solvent on benzaldehyde and acetophenone hydrogenation is shown in Table 2. In general, alcohols are comparatively desirable solvents, while toluene is not a good solvent, especially in the hydrogenation of acetophenone.

As shown in Figs. 3 and 4, the hydrogenation rates were greatly affected by change in temperature. No matter which catalyst is used, the most suitable temperature for benzaldehyde hydrogenation is at 30–40°C, and that for acetophenone hydrogenation is at 50–60°C. Raising the temperature above the appropriate points decreases the rate of hydrogenation.

Benzaldehyde and acetophenone can be converted to benzyl alcohol and α-phenylethanol in 100% yields by these two catalysts at room temperature and atmospheric pressure. Table 3 shows the stabilities of these two complexes in the recycling processes. As can be seen, these two catalysts are very stable and can be reused.

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References

1 B.R. James, Homogeneous Hydrogenation, Wiley, New York, (1973).
2 W. Strohmeier and L. Weigelt, J. Organometal. Chem., 145 (1978) 189.
3 R.A. Sanchez-delgado and O.L. De Ochoa, J. Mol. Catal., 6 (1979) 303.
4 P. Frediani and U. Matteoli, J. Organometal. Chem., 150 (1978) 273.
5 N.J. Holy, J. Org. Chem., 44 (1979) 239.
6 Y.Z. Zhou and Y.Y. Jiang (Chiang), Polymer Preprints, Japan, 28 (1979) 2018.
7 Y.Z. Zhou and Y.Y. Jiang (Chiang), Polymer Comm., China, (1979) 97.
8 H.S. Bruner and J.C. Bailar, Jr., Inorg. Chem., 12 (1973) 1465.