CHEMISTRY LETTERS, pp. 1215 - 1218, 1984.

GAS-PHASE HYDROFORMYLATION OF ETHYLENE OVER SUPPORTED PALLADIUM CATALYSTS AT ATMOSPHERIC PRESSURE

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The palladium-exchanged silica catalysts have almost the same activities as the rhodium catalyst in the gas-phase hydroformylation of ethylene at 50-110 °C and 1 atm.

In the heterogeneous hydroformylation of olefin to aldehyde, rhodium has been noted as an excellent catalyst. Heterogeneous Pd catalysts have, however, been little used for this reaction except for the Pd-Co complex catalyst.1) The present study shows that simple Pd-exchanged silica catalysts have activities for ethylene hydroformylation similar to those of Rh catalysts reported in earlier papers, though hydrogenation proceeds to a large extent. Conventional supported Rh catalysts prepared by $RhCl_3$ impregnation2,3) show little activity for hydroformylation after hydrogen-reduction. In the present study, however, Pd catalysts prepared by $PdCl_2$ impregnation show activity after hydrogen-reduction. The Pd-exchanged silica catalysts exhibited no activity for hydroformylation without the hydrogen-reduction. The catalysts employed in the present work, were all reduced by means of a hydrogen-flow (60 ml/min) for 2 h.

For the catalyst preparation by cation exchange (EX in catalyst name), an aqueous solution of $Pd(NH_3)_2Cl_2$ was used. Silica gel (BET surface area:280 m^2/g, SL in catalyst name) and silica-alumina4) (SA in catalyst name), were previously treated with an ammonia aqueous solution. Na-Y zeolite5) (Z in catalyst name) was previously treated with NH_4Cl saturated aqueous solution. After exchange, the catalysts were washed with water until no chlorine ion was detected, and then the catalysts were dried at 100 °C. All these catalysts were light yellow. The same silica gel as described above and alumina6) were used for the catalyst preparation by impregnation (IMP in catalyst name).

The Pd content was determined by means of chelatometry. Seven kinds of catalysts were prepared and summarized in Table 1.

Ethylene hydroformylation was performed in an atmospheric-flow reactor made by a U-shaped Pyrex glass tube with 8 mm in inner diameter. In all the experimental conditions, 1.3 g of catalysts were loaded and the flow rate of reactant gas (C_2H_4 : CO : H_2 =1:1:1 mol ratio) was 60 ml/min at room temperature. Water was removed from all these reactant gases by the use of a dry-ice trap. The gaseous products were cooled in the dry-ice trap, and propionaldehyde (C_3H_6O) was periodically collected and analyzed by means of gas chromatography.

Table 1. Catalyst names

Catalysts	Pd contents (mg-atom Pd/g-cat.)
Pd-SL-EX1	0.185
Pd-SL-EX2	0.093
Pd-SL-IMP	0.179
Pd-AL-IMP	0.198
Pd-SA-EX1	0.730
Pd-SA-EX2	0.185
Pd-Z-EX1	1.08

C_3H_6O and ethane (C_2H_6) were formed as the main products. CO_2 and CH_4 were also formed in a negligible quantity.

Typical changes in C_3H_6O and C_2H_6 formation with time on stream are shown in Fig. 1. Pd-SL-EX1 and Pd-SL-IMP were reduced at 300 °C and evacuated at 300 °C for 2 h. At the initial stage in the reaction using the fresh Pd-SL-EX1 catalyst at 70 °C, the rate of C_3H_6O formation (r_{PA};mmol/min g-atom Pd) increased and the rate of C_2H_6 formation (r_E;mol/min g-atom Pd) decreased with the reaction time for 3 or 4 h, and a steady state then followed. This period of rising r_{PA} was shortened by recommencing the reaction after holding the catalyst in non-mobile reactant gases at room temperature overnight. In the case of a low Pd content (Pd-SL-EX2) or at the reaction temperature above 70 °C, this period was less than 2 h. In the Rh-zeolite catalysts, there are very different data of such induction periods as 4 h[2)] and more than 10 h[7)]. All the catalysts prepared by impregnation showed the decreasing r_{PA} for initial 4 or 5 h, and a steady state then followed like Pd-SL-IMP in Fig.1. The results described below were obtained from the reaction in the steady state.

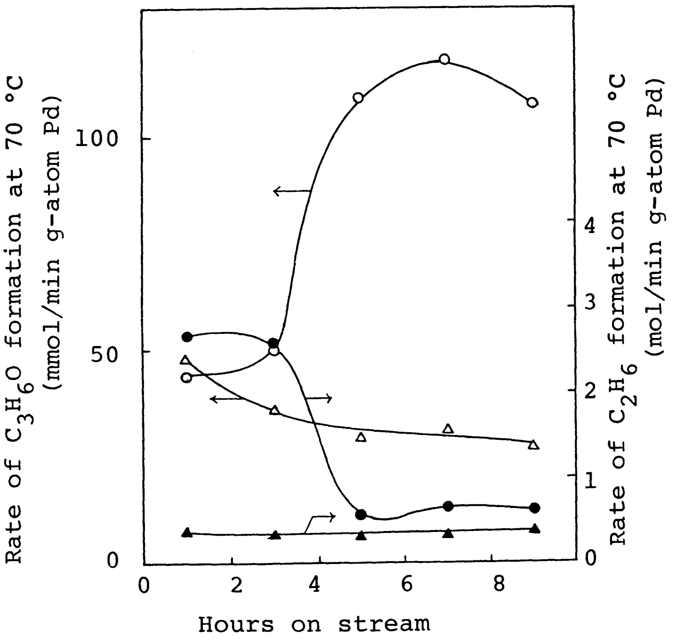

Fig. 1. Hydroformylation on Pd/SiO_2.
○ , ● :Pd-SL-EX1 300 °C calcination.
△ , ▲ :Pd-SL-IMP 400 °C calcination.

Table 2. summarizes the effects of various pretreatments. Calcinations were performed in air at 300 °C for 2 h and reductions were performed in hydrogen flow 60 ml/min for 2 h at various temperatures t_H °C. Evacuations were performed below 0.001 Torr for 2 h at the same temperature as t_H. The reaction temperature was 70 °C. When the evacuation was not performed, r_{PA} were small and r_E were large in the same conditions. The calcinated catalysts have larger r_{PA} and smaller r_E than the catalysts without the calcination in the same reduction temperature except for 200 °C. On the basis of the data (Table 2), subsequent pretreatments were always carried out as described below. The calcinations were performed for 2 h in air, at 300 °C for the exchanged catalysts and 400 °C for the impregnated catalysts respectively. The catalysts were always reduced at 300 °C and evacuated below 0.001 Torr for 2 h at 300 °C.

The temperature dependencies of the r_{PA} and the r_E are shown in Fig.2. The r_E increases rapidly with increasing temperature and in the range of this rapid rise the r_{PA} shows rather sharp maxima. The low Pd content catalyst (Pd-SL-EX2) has a maximum in the higher temperature. There is no great difference in the maximal r_{PA} between the two kinds of the exchanged catalysts. The maximal r_{PA} of the impregnated catalyst (Pd-SL-IMP) is less than half those of the exchanged catalysts. In the cases of other supports, the temperature dependencies of r_{PA} and r_E had similar tendencies to that shown in Fig.2.

The difference of r_{PA} in the preparation between impregnation and exchange is suggestive of a comparison of the metal dispersion. As a measure of the dispersion, the irreversible adsorption values of CO and H_2 on the fresh catalysts were determined at room temperature. The conditions of pretreatment were the same as in the reaction. These data are summarized in Table 3 with the maximal r_{PA} and r_E in the same condition. There is no correspondence between the maximal r_{PA} and the irreversible adsorption values of CO and H_2 over the whole supports.

Strong acidic supports like silica-alumina and zeolite are ineffective for hydroformylation.

The maximal r_{PA} on the Rh catalysts reported in earlier papers were calculated to have identical (mmol/min g-atom Rh) dimension. The r_{PA} of 3.7 wt%[8)] and 0.79 wt%[7)] Rh-zeolite are 78.8 and 12.1, respectively. For the catalysts prepared from Rh-complex, r_{PA} of 3.1

Table 2. The effect of pretreatment on the activities of Pd-SL-EX1

	t_H	r_{PA}	r_E
Calcinated	200	71.7	0.661
at 300 °C	250	90.2	0.671
	300	107.7	0.605
	$300^{c)}$	$26.1^{c)}$	$2.60^{c)}$
No calcination			
	150	21.1	0.294
	$150^{c)}$	$25.3^{c)}$	$0.295^{c)}$
	200	78.4	0.979
	250	66.6	2.56
	300	59.8	2.62
	$300^{c)}$	$22.8^{c)}$	$2.86^{c)}$

c) No evacuation.

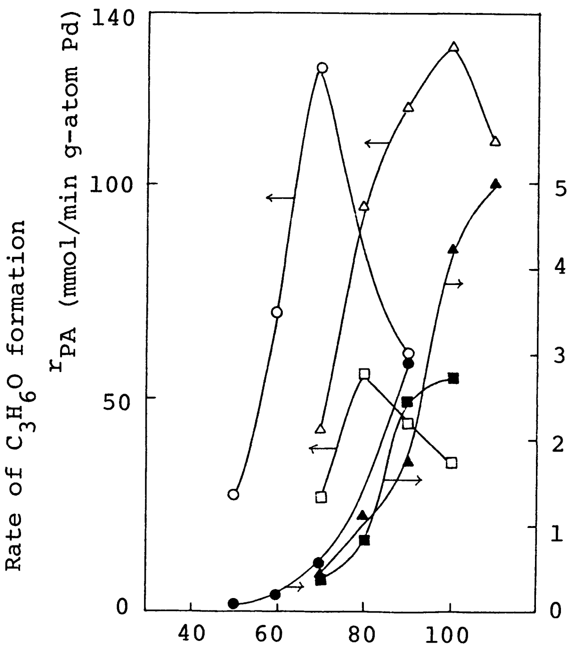

Fig.2. Temperature dependencies.

○ , ● :Pd-SL-EX1, △ , ▲ :Pd-SL-EX2

□ , ■ :Pd-SL-IMP.

Table 3. Summary of various catalysts

	t_R	r_{PA} a)	r_E	CO b)	H_2 b)
Pd-SL-EX1	70	107.7	0.605	0.65	0.34
Pd-SL-EX2	100	132.6	4.23	0.30	0.10
Pd-SL-IMP	80	55.6	0.844	0.21	0.13
Pd-AL-IMP	80	52.7	0.595	0.44	0.26
Pd-SA-EX1	65	10.8	0.150	0.18	0.14
Pd-SA-EX2	80	25.9	0.478	0.35	0.20
Pd-Z-EX1	60	1.2	0.313	0.06	0.06

t_R :reaction temperature (°C). a) Maximal values.
b) mol/g-atom Pd.

wt% Rh/SiO_2 9) and 0.25 wt% $Rh_4(CO)_{12}$-ZnO 3) are 23.8 and 164.6, respectively. While the comparison of the maximal r_{PA} between Pd and Rh under the conditions of the same preparation and supports is impossible, the maximal r_{PA} in Table 3 except for Pd-Z-EX1 are almost the same as those reported by earlier investigators. The maximal r_{PA} of Pd-Z-EX1 is smaller than those of Rh-zeolite catalysts 7,8) in spite of the same cation exchange preparation. This is attributable to the different forms of cation such as Rh^{3+}, Na^+-Y, $Pd(NH_3)^{2+}$, and NH_4^+-Y. Detailed study of these problems will be continued.

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(Received April 18, 1984)