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Polymer Catalysts

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ABSTRACT

Catalysts of reduced and unreduced PdCl_2 with hydrazine hydrate deposited on polyaminochloroquinones or polyaminochlorohydroquinones were obtained. Polyaminochloroquinones were prepared by solution polycondensation of chloranil with benzidine in the presence of an acceptor, sodium acetate, for the resulting hydrochloric acid. Polyaminochlorohydroquinones were obtained by a reduction reaction of polyaminochloroquinones with 2,2'-diphenylhydrazine. The polymer catalysts were tested in the styrene hydrogenation reaction. The polymers and polymer catalysts were studied by IR spectroscopy.

INTRODUCTION

Mineral compounds have been very good catalysts for increasing chemical reaction rates. In the last few years several articles dealing with catalytically interesting properties of some synthetic polymers

have been published. They are used in both heterogeneous and homogeneous catalyst fields. Supported homogeneous catalysts which include the advantages of homogeneous and heterogeneous catalysts have recently been synthesized. Natural and synthetic polymers have long been used to stabilize the colloidal metals of Group VIII. The behavior of polymer supported metals is similar to that of colloidal metals or that of inorganic supported metals. However, the use of polyamide as a support for platinum displays an interesting selectivity for 1) the hydrogenation of benzene to cyclohexene [1] and 2) the hydrogenation of styrene to ethylbenzene [1]. In the first case it has been demonstrated that this selectivity is determined by the geometric arrangement of platinum atoms corresponding to the arrangement of the amide groups.

The activity and selectivity of the polyamide platinum catalyst depends on the nature of the polymer. Thus, platinum anchored on polyamide 66 and 610 catalyzes the formation of cyclohexene, whereas polyamide-3 platinum, although active, affords only cyclohexane.

In the second case the catalytic activity did not depend on the total content of platinum but rather seemed to be proportional to the amount of platinum at the surface of the polyamide. These results were interpreted in terms of diffusion on the Pt-compound during impregnation of the beads.

Catalysts of PdCl_2 deposited on polyaminochloroquinones were studied in an earlier paper [2] on the test reaction of styrene hydrogenation.

Generally, the main products of styrene hydrogenation are ethylcyclohexane and/or ethylbenzene. In early experiments with the polyaminochloroquinones, 0.05 to 0.5% palladium catalysts were used. That content of palladium influences the conversion of styrene to ethylbenzene; i.e., an increase of the palladium content leads to an increase of styrene conversion to ethylbenzene.

The use of a polymeric support of the polyaminochloroquinone type increases the selectivity of palladium because hydrogenation of styrene is realized only in a vinyl chain. By the reduction of palladium chloride that was deposited on a polyaminochloroquinone with hydrazine hydrate, a catalyst was obtained which, in the same hydrogenation reaction test, had a lower catalytic activity.

It was thought that the reduction of palladium chloride with hydrazine hydrate causes the partial reduction of the polyaminochloroquinone used as a support, and this reduced form is detrimental to catalytic activity. For this reason we have studied the catalytic activity of polymers in oxidized and reduced forms with PdCl_2 deposited on the polymer.

EXPERIMENTAL

Polycondensation of Chloranil with Benzidine

The chloranil-benzidine polymer has been prepared according to the procedure of Berlin [3], but in more diluted solutions and with a modified washing procedure to obtain more pure polymer.

To a three-necked, round-bottomed flask (1000 mL) equipped with a mechanical stirrer, a funnel, and a reflux condenser was introduced chloranil (2.45 g, 10 mmol) in ethyl alcohol (500 mL). It was dissolved under stirring and was heated to reflux. Then the benzidine (1.84 g, 10 mmol) dissolved in ethyl alcohol (400 mL) was added, followed by the entire quantity of powdered sodium acetate. The reaction mixture was refluxed for 2 h, hot filtered, and dried at 105°C in a drying chamber. The dry powdered polymer was washed with ether (500 mL) in the same reaction flask for 1 h at room temperature with stirring to remove the unreacted chloranil. Purification was completed by repeated washing of the polymer with water (500 mL) by stirring at reflux to remove inorganic salts, and with ethyl alcohol (500 mL) to remove the unreacted benzidine and low molecular weight, minor products. Pure polymer, 2.9383 g (75% yield), was obtained.

Reduction of Polyaminochloroquinones

Polyaminochlorohydroquinones have been obtained by the reduction of polyaminochloroquinones with diphenyl hydrazine. For this purpose, polyaminochloroquinone (75 g, 2 mmol) was introduced into a 100-mL Erlenmeyer flask in which was dissolved 2,2'-diphenylhydrazine (1 g, 5 mmol) in ether (50 mL). The mixture was kept at room temperature for 2 h. After filtering, the reduced polymer was washed with ether until it became colorless.

Catalyst Preparation

The catalysts were prepared by impregnating polymers with aqueous hydrochloric solutions of PdCl₂. The polymer (2.27 g, 6 mmol) was placed in a vessel with a solution of PdCl₂ (0.0115 g Pd for catalysts with 0.5 wt% Pd) and allowed to stand overnight.

Half from the solid product obtained was separated, washed with water, and dried at 110°C. In this way the polyaminochloroquinone-PdCl₂ and polyaminochlorohydroquinone-PdCl₂ catalysts were obtained.

The next portion of solid product was reduced with hydrazine hydrate in alkaline medium. For that, the solution was adjusted to about pH 9 by the addition of KOH solution, and then hydrazine hydrate in excess was slowly added until the metal was completely reduced. The brown mass was washed with water to remove the alkalinity and dried at 110°C. This resulted in two kinds of catalysts: the polyaminochloroquinone and polyaminochlorohydroquinone with deposited PdCl₂, and the same compounds reduced.

Testing of Catalytic Activity

The activities of the catalysts were tested by the hydrogenation reaction of styrene. The reaction was carried out in a 5- μ L pulse micro-

reactor. The reaction products were analyzed on a Chromatron gas-chromatograph GCHF 18.3 fitted with a catharometer. The column (1 m in length, 0.11 in. in diameter) was packed with 10% tricresylphosphate on Chromosorb P 30-60 mesh. The injector, column, and detector temperatures were 100, 80, and 100°C, respectively. The hydrogen flow rate was 86 mL/min. For each determination, 0.14 g catalyst was used.

RESULTS AND DISCUSSION

The following abbreviations are used: PACQ-PdCl₂ = catalyst obtained from polyaminochloroquinone by deposition of PdCl₂, PACQ-PdCl₂ (r) = catalyst obtained from polyaminochloroquinone by deposition of PdCl₂ and their reduction with hydrazine hydrate, PACHQ-PdCl₂ = catalyst obtained from polyaminochlorohydroquinone by deposition of PdCl₂, and PACHQ-PdCl₂ (r) = catalyst obtained from polyaminochlorohydroquinone by deposition of PdCl₂ and their reduction with hydrazine hydrate.

The results obtained in testing the above catalysts are presented in Fig. 1.

Examination of Fig. 1 reveals that catalytic activity is a function of the use of polyaminochloroquinones or polyaminochlorohydroquinones as supports and by the use of reduced and unreduced PdCl₂ deposited on the support. In the first case, the use of the PACQ-PdCl₂ catalyst, the catalytic activity begins at 60°C and the conversion of styrene to ethylbenzene increases with an increase in temperature, so that at 90°C the conversion is 100%. Only ethylbenzene is present as a reaction product.

PACHQ-PdCl₂ catalyst has similar behavior in the same hydrogenation reaction test. Conversion increases with an increase in temperature; maximum conversion is obtained below 110°C.

The PACQ-PdCl₂ (r) catalyst presents a different behavior. Catalytic activity begins at 50°C, increases up to 70°C (maximum conversion 80%), and decreases up to 120°C.

PACHQ-PdCl₂ (r) catalyst gave unexpected catalytic activity. The catalyst attains maximum conversion at low temperature (40°C) while maintaining the same high selectivity.

The best catalytic activity is that of the PACHQ-PdCl₂ (r) catalyst. The PACQ-PdCl₂ and PACHQ-PdCl₂ catalysts show comparable catalytic activities. The PACQ-PdCl₂ (r) catalyst has the least catalytic activity.

The structures of these catalysts are interesting. For the polymer based on chloranil and benzidine, Berlin [3] indicated the formation of a copper chelate which contains Cu-N bonds but not Cu-Cl bonds. In the case of the catalysts presented above, the substitution of hydrogen for amino groups with palladium may not be produced by using a weakly acidified palladium chloride solution for complexation. It is more

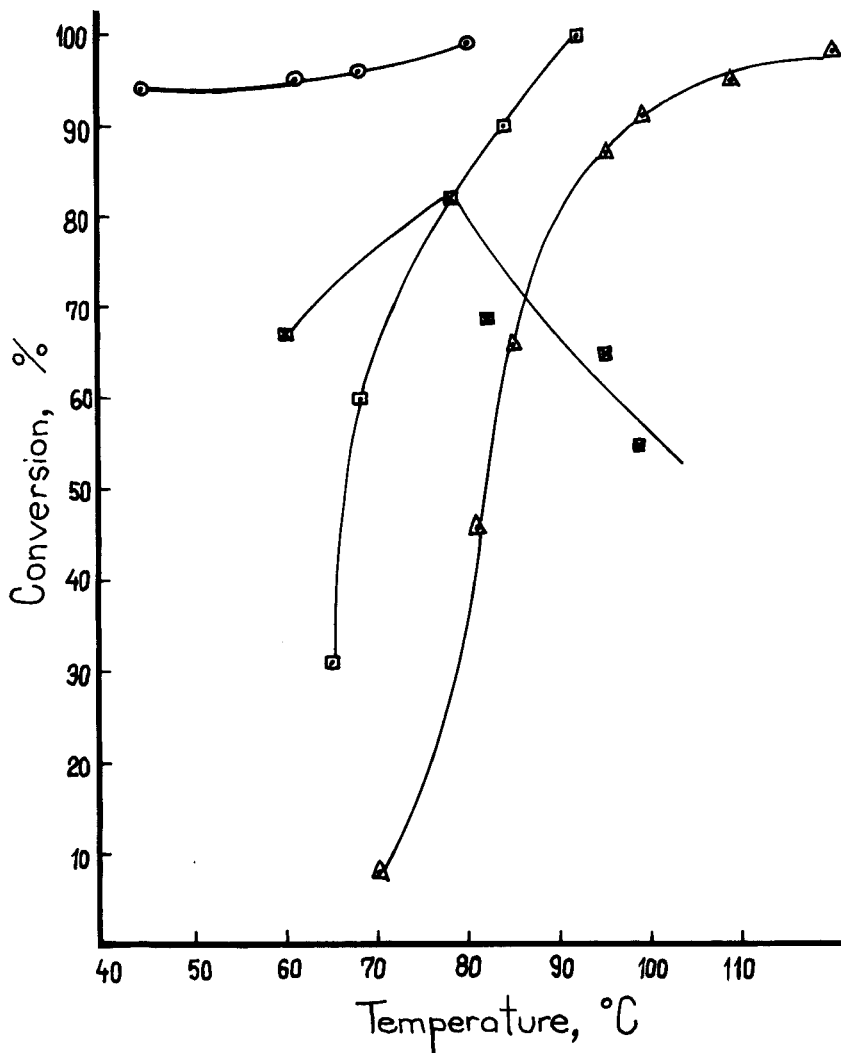


FIG. 1. The catalytic activity of polymer catalysts in test reactions of styrene hydrogenation: (△) PACHQ-PdCl₂, (○) PACHQ-PdCl₂ (r), (□) PACQ-PdCl₂, (⊗) PACQ-PdCl₂ (r).

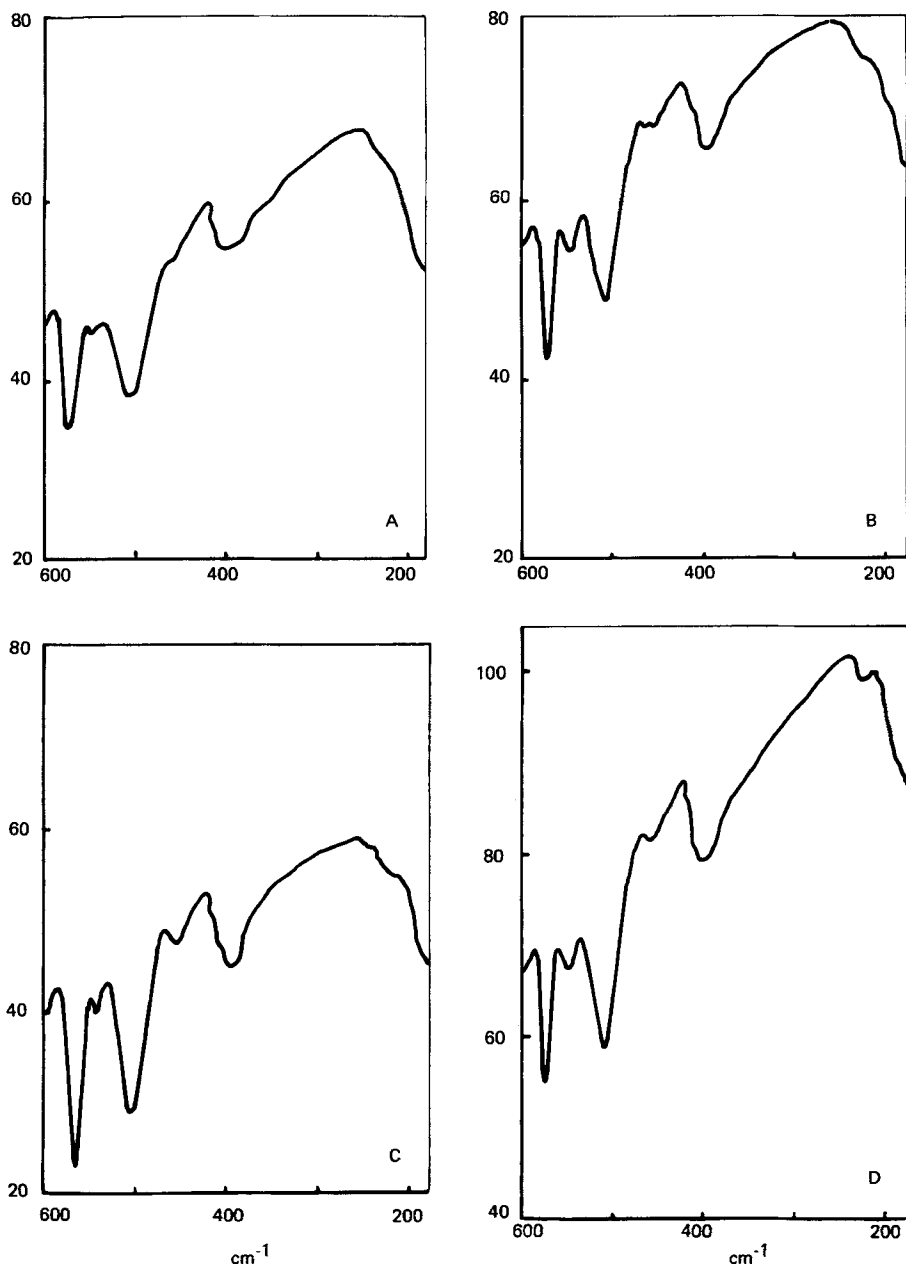


FIG. 2. IR spectra of polymer catalysts: (A) PACQ-PdCl₂ (r), (B) PACQ-PdCl₂, (C) PACHQ-PdCl₂, (D) PACHQ-PdCl₂ (r).

probable that the palladium chloride and the amino groups of the polymer support form a complex similar to the complex of palladium chloride with ammonia. This assumption is supported by the IR spectra of the catalysts in the 200-600 cm^{-1} region (Fig. 2).

Note that the Pd-N stretching frequency is at 508 cm^{-1} for all catalysts. This is in agreement with the data of During [4] who found that the Pd-N stretching frequency ranges from 528 to 436 cm^{-1} , depending on the nature of the ligands in the complex. From Fig. 2 it is seen that the characteristic band for Pd-Cl appears at 360 cm^{-1} , thus proving the presence of this bond [5].

The IR spectra indicate the presence of a single active species of catalyst in which catalytic activity increases or decreases depending on other structures present in the reaction mixture.

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