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CATALYTIC ACTIVITY AND THE GLASS TRANSITION OF POLYMER-BOUND METAL COMPLEX CATALYST

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Rhodium(I)-complex was bound on a ternary copolymer of styrene (ST), divinyl benzene (DVB) and diphenyl-p-styrylphosphine (DPSP). The hydrogenation of ethylene was studied over this polymer-bound metal complex, at 40∽90 °C in gas phase. The catalytic activity changed abruptly at around 68 °C due to the reversible discontineous change in the pre-exponential factor, which was ascribed to the glass transition of the polymer.

Many research efforts have been devoted to the studies on the polymer-bound metal complex catalysts$^{1)}$. These polymer complex catalysts can be considered as simple models for enzyme catalysts, and expected to provide a key to understand the nature of bio-catalysts and also a way leading to their application for the catalyst design.

One of the most advanced studies was concerned with the polymer-bound Wilkinson type complexes, i. e., tris(triphenyl phosphine)chlororhodium(I). In the early developed procedure, polystyrene was functionalized by chloromethylation$^{2)}$, and then the phosphine links were introduced.

In the present study, however, a polymer-bound metal complex catalyst was prepared by the following procedure. Diphenyl-p-styrylphosphine was prepared according to Rabinoviz's method$^{3)}$. A crosslinked copolymer was prepared from a mixture of ST, DVB and DPSP by the suspension polymerization technique under nitrogen atmosphere, using α, α'-azobis-isobutyronitrile (AIBN) as an initiator, where the ratio of monomers was ST:DVB:DPSP = 93:2:5. The polymer (7.5g) was treated with 1.62g of Wilkinson complex in 70 ml of benzene at room temperature for two weeks under nitrogen atmosphere. The polymer-bound complex thus prepared was washed with benzene and then with dichloromethane. The solvents contained in the catalyst were removed further by evacuation at room temperature. The content of rhodium in the polymer-bound complex was 0.14 mmol/g as determined by gravimetry after calcination.

This complex catalyst was found to be active in gas phase reactions for the isomerization of n-butenes, and the hydrogenation of ethylene, propylene or n-butenes at 60 °C$^{4)}$.

The hydrogenation of ethylene was carried out over about 1 g of the catalyst which was pre-evacuated at 70 °C or 90 °C for 15 min. The rate of the reaction was followed by measuring the pressure decrease and also by the gas phase analysis with a gas chromatograph. The treatment of evacuation reproduced the catalytic activity at constant level over ten runs. The reaction was found to follow the rate expression:

$$r = k\ P_{C_2H_4} \cdot P_{H_2}^{0.3}$$

Figure 1 shows the temperature dependency of the catalytic activity. It is obvious that the Arrhenius plot can be divided into two regions at around 68 °C. The activation energy obtained from either slope was 8.5 kcal/mol and independent of the pretreatment temperatures and of the history of the catalyst. For example, the catalytic activity of run 7 was similar to that of run 3, though the former is concerned with the catalyst which had been subjected further to the different pretreatments and reaction conditions. Thus, the change in the catalytic activity was reversible.

The glass transition temperatures of non-crosslinked polystyrene were reported to be 80∼90 °C[5], which depend on the degree of polymerization and the fine structure of the polymer. Further, in the case of the crosslinked polymer, the temperature may also depend on the extent of crosslinking. The results with DSC (differential scanning calorimetry) and TG proved that a similar type of copolymer, e. g., ST-DPSP-ethyleneglycoldimethylacrylate, showed a clear endothermal peak around 67∼75 °C without any detectable weight loss. The copolymer of ST-DVB-DPSP and the polymer-bound complex catalyst showed very small peaks at around 80 °C, which can be attributed to the glass transition of these polymers. The glass transition temperature observed in DSC experiments is higher than the temperature of the "discontinuity" in the catalytic activity. Since, the DSC peaks shift to higher temperatures on increasing scanning speed, the discrepancy seems to be due to the higher rate of temperature increase in DSC experiment. In conclusion, the drastic change in the catalytic activity of the polymer-bound metal complex can be ascribed to the glass transition of the polymer.

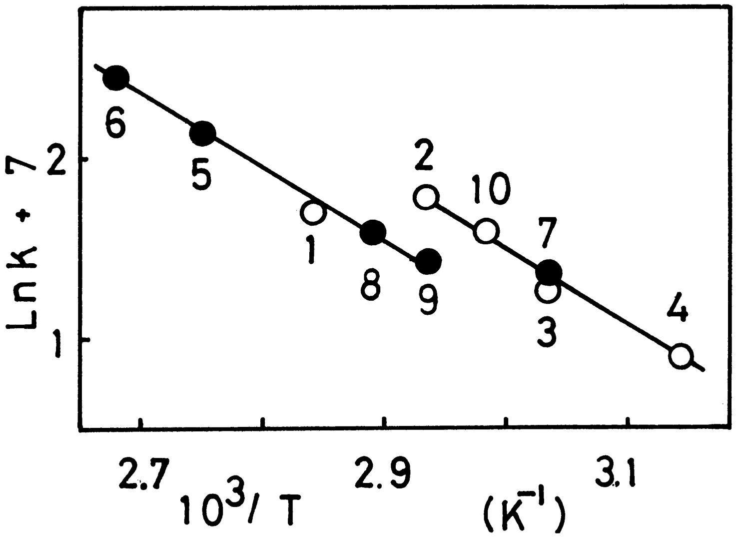

Fig.1. Arrhenius plots for the hydrogenation of ethylene over the polymer-bound Rh(I)-complex. The catalyst was pre-evacuated befor each run, at 70 °C (open circles) or at 90 °C (closed circles). The initial pressures of C_2H_4 and H_2 were 204 Torr. Numbers in the figure indicate the run number.

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