Effect of cross-linking on catalytic performance of polystyrene supported platinum carbonyl clusters

Himadri Paul1, Sumit Bhaduri1* & Goutam Kumar Lahiri2*

1Reliance Industries Limited, Chitrakoot 1st Floor, Sri Ram Mills Compound, Ganpatrao Kadam Marg, Worli, Mumbai 400 013, India
Email: sumit_bhaduri@ril.com

2Department of Chemistry, Indian Institute of Technology-Bombay, Powai, Mumbai 400076, India
Email: lahiri@chem.iitb.ac.in

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Commercial chloromethylated divinylbenzene cross-linked polystyrene resins (5.5% and 8%) have been functionalized by the reaction with triethylamine. The Chini cluster \([\text{Pt}_3(\text{CO})_9]^{2-}\) has been anchored onto the resultant materials by anion exchange. The degrees of functionalization in terms of chloromethyl and benzyltriethyl ammonium functionalities are found to be very high and high (>85% and >60%) respectively for both the polymers. The total platinum content of the 8% cross-linked polystyrene is a little (~13%) more than that of 5.5% cross-linked polymer. The catalytic activities of the resultant materials after mild thermal activation have been studied for the hydrogenation of a variety of unsaturated compounds. The substrates studied are: cyclohexanone, acetophenone, methyl pyruvate, ethyl acetooacetate and nitrobenzene. For most of the substrates the activity of the 5.5% cross-linked material is found to be a little more than that of the 8.8% cross-linked material. This is despite the fact that the latter has more platinum both in the bulk and on the surface as measured by atomic absorption and EDAX (SEM) techniques respectively. After functionalization with cinchonine and \([\text{Pt}_3(\text{CO})_9]^{2-}\), both the polymers have been tested as possible asymmetric catalysts for the hydrogenation of methyl pyruvate. No enantioselection is observed and a tentative explanation is offered for the lack of enantioselection.

Transition metal complexes adsorbed on insoluble polymeric materials, or bound to them through pendant ligands have been much investigated as potential catalysts1. Compared to soluble homogeneous catalysts at the end of a catalytic run supported catalysts can be easily separated and recycled. Supported polynuclear carbonyl complexes are known to generate small metal crystallites of novel catalytic properties2. Therefore, catalysts made by carbonyl clusters supported on inorganic or organic polymeric materials have received considerable attention in recent years1,2. While for anchoring carbonyl clusters majority of the supports has so far been inorganic oxides, there are some reports where functionalized organic polymers have also been used.

We have reported the reaction of the Chini clusters, \([\text{Pt}_3(\text{CO})_9]^{2-}\) (n = 3,4,5), with dihydrogen and the potential use of such reactions in homogeneous and supported catalytic systems3,4,5. The use of commercial anion exchange resin as a support material for a number of anionic carbonyl clusters including the Chini clusters were reported by us many years ago3. Later on this method of ion-pairing Chini clusters on suitable supports was found to be of special interest because of the ability of the resultant materials to catalyze hydrogen driven reductions of redox active bimolecules, and asymmetric hydrogenation of methyl pyruvate4,5.

The degree of cross-linking, the degree of functionalization and the pore size distribution of an anion exchanger are expected to influence the overall performance of the catalyst derived from it. The work reported here was undertaken to investigate these aspects in some detail.

Materials and Methods

Chloroplatinic acid was purchased from Johnson Matthey, London. 5.5% Merifield polystyrene, methyl pyruvate, methyl L-lactate were purchased from Fluka, Switzerland. 1-Phenylethanol and ethyl-3-hydroxy butyrate were obtained from Aldrich, U.S.A. Nitrobenzene, cyclohexanone, cyclohexanol, ethylacetooacetate, acetophenone, triethylamine and other organic solvents used in this work were procured from S. D. Fine, India. 8% Cross-linked polystyrene resin was a gift sample from Ion-Exchange, India.
Physical measurements

Atomic absorption measurements were carried out on GBC 902 double beam atomic absorption spectrophotometer. Microanalyses were carried out with a Carlo Erba 1106 model (Italy) C, H, N analyzer. The anionic carbonyl cluster \([\text{Pt}_{15}(\text{CO})_{30}]^{2-}\) (1) was synthesized according to the literature procedure. Hydrogenation experiments were carried out in an autoclave. Hydrogenation of all substrates were monitored by gas chromatography (GC) using a SC-30 (mesh 1000-2000) GC column with FID detector. Porosity and surface area measurements were done using mercury porosimetry and a BET surface area analyzer. IR spectra were taken on a Nicolet Impact 400 spectrometer. Scanning Electron Micrographs were recorded in Camaca model 2003 instrument. All the solvents were dried and distilled under nitrogen prior to use. All the reactions were carried out under nitrogen atmosphere unless otherwise stated.

(A) Functionalization of the polymer

A mixture of chloromethylated 5.5% DVB cross-linked polystyrene beads (1 g) and triethylamine (10 ml) or cinchona alkaloid (1.0 g) was stirred in toluene (40 ml) [in case of cinchona a mixture of toluene-methanol (v/v, 1:1) was used] at 100°C for 24 h. The polymer beads were filtered off and washed successively with methanol, chloroform and ether and then dried under vacuum. The same procedure was followed for the functionalization of 8% DVB cross-linked polystyrene.

Microanalytical data for 5.5% cross-linked polystyrene (observed): C, 72.2; H, 6.3; N, 0.0 and microanalytical data after functionalization with NEt₃ (observed): C, 65.4; H, 8.8; N, 4.2.

Microanalytical data for 8% cross-linked polystyrene (observed): C, 71.2; H, 6.3; N, 0.0 and microanalytical data after functionalization with NEt₃ (observed): C, 59.5; H, 9; N, 3.2.

(B) Synthesis of (2) and (3)

To a green solution of \(\text{Na}_2\text{Pt}_{15}(\text{CO})_{30}\) (0.1 g) in methanol (10 ml) chloromethylated 5.5% DVB cross-linked polystyrene beads quaternized with triethylamine or cinchonine was added and the mixture was stirred at 25°C for 12 h under nitrogen. This resulted in a pale green solution and dark green beads of 2. The beads were filtered off, washed thoroughly with methanol and vacuum dried. Catalyst 3 was prepared by following the same general procedure.

(C) Decarboxylation of 2 and 3, kinetic studies and recarboxylation

For a typical catalytic experiment, 2 (0.1 g) was heated at 80°C under vacuum for 4 h. The IR spectrum of a portion of the solid showed the total disappearance of the inorganic carbonyl bands. A methanol solution (5 ml) of methyl pyruvate (amount varying to give a concentration between 0.25 and 10 mol/l) and catalyst in a glass vial with a small magnetic bar was placed in the autoclave of 250 ml capacity. The reactor was charged with 500 psi of H₂ and the solution in the vials were stirred magnetically at 25°C for various lengths of time. The conversion of methyl pyruvate to methyl lactate was measured by gas chromatography.

The same procedure was followed for all other substrates.

Results and Discussion

(A) Preparation and characterization of the precatalyst

In the work presented here two commercial chloromethylated polystyrene resins, cross-linked with 5.5 and 8% divinylbenzene (DVB), have been reacted with triethyl amine to give benzyltriethyl ammonium functionalities on the surface. As shown in Scheme 1, the chloride anions of the resultant anion exchangers may then be substituted with \([\text{Pt}_{15}(\text{CO})_{30}]^{2-}\) (1) to give (2) and (3). This is effected by the treatment of the functionalized supports with methanolic solutions of the sodium salt of (1) followed by repeated washing of the resultant material with methanol to remove all physically adsorbed sodium salt of (1). Such washing is expected to remove all physically adsorbed (1) unless it is entrapped within the pores of the polymer. It may be noted that the material derived from 5.5% cross-linked resin, (2) has been schematically formulated somewhat differently from that derived from 8% cross-linked resin. The evidences for both these formulations are discussed below.

The evidence for the successful functionalization comes from the nitrogen and platinum analytical data. Expectedly nitrogen analysis of the parent chloromethylated resins show zero nitrogen while after the treatment with NEt₃ reproducible amounts of nitrogen are found in both the resins. Similar observations are made for platinum analytical data.
before and after treatment of the functionalized resins with (1). To differentiate between bulk and surface platinum concentrations, platinum analyses of (2) and (3) have been performed by atomic absorption and SEM (EDAX) methods.

The evidence for the retention of molecular identity by (1) in (2) and (3) is based on IR spectra. The anion (1) is known to have characteristic IR bands for terminal and doubly bridging carbonyl groups. As shown in Fig. 1, (2) has IR signals that match well with those of (1), and although not shown, identical IR spectra are also obtained with (3). These observations are in agreement with our earlier work on similar supported systems.

In Scheme 1 for (2) one cluster anion is shown to pair up with two quaternary ammonium groups. To maintain electroneutrality, the cluster dianion must ion pair with two singly charged cations. As already mentioned, the anion exchange between Cl⁻ and (1) is effected by the treatment of the functionalized polystyrene with the sodium salt of (1). Repeated analyses either by atomic absorption or by EDAX do not show the presence of detectable amounts of sodium in (2). The absence of sodium implies that (2) does not contain any physically adsorbed sodium salt of (1). It also implies that an alternative formulation in which one cation is the quaternary ammonium group and the other is a sodium ion, if present would be negligible in amounts. This however is not the case with (3) where sodium is detected on the surface by EDAX (see Table 1). This is the rationale for having both the formulations for (3) in Scheme 1.

Microanalytical data (C, H, N) and % Pt of (2) and (3) at different stages of preparation of the supported species have been used for determining the degree of functionalization. These values are given in Table 1, and may be interpreted as follows. The 5.5 and 8% cross-linked resins before functionalization has 55 and 80 divinylbenzene units for every 945 and 920 units of styrene respectively. In (2) out of a thousand monomeric units approximately 870 have chloromethyl functionality. Out of these 870 units about 650 are quaternized by triethylamine and only six out of these 650 take part in ion pairing with three cluster anions i.e. (1).

The analytical data of (3) indicates a very similar picture. Here both the numbers of chloromethylated groups as well as the number of quaternary ammonium containing functionalities are a just little more. In the chloromethylated polymer about 900 monomeric units have chloromethyl functional groups and on treatment with NEt₃ out of these 900 units, 700 units are quaternized. However, like with (2) very few of these quaternary ammonium groups, at the most eight out of 700 units, ion pair with four of (1). One of the reasons for this relatively low fraction of quaternary ammonium group taking part in ion pairing with (1) in both (2) and (3) may be that, to be
Table 1—Functionalization, EDAX and porosity data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Functionalization (%)</th>
<th>Total Platinum ( % by AAS)</th>
<th>Surface Elemental concentration (EDAX)</th>
<th>Pore size distribution</th>
<th>Surface area m²/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&quot;Chloro&quot; functionality</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>87</td>
<td>65</td>
<td>0.3</td>
<td>Pt: 0.7 to 1.25</td>
<td>~87% of relative volume is from pores having diameter between 10 to 60 Å.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cl: 0.94 to 1.05</td>
<td>33% is from 10 to 20 Å.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na: Nil</td>
<td>~62% of relative volume is from pores having diameter between 10 to 60 Å.</td>
</tr>
<tr>
<td>(3)</td>
<td>90</td>
<td>70</td>
<td>0.4</td>
<td>Pt: 0.7 to 1.65</td>
<td>19% is from 10 to 20 Å.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cl: 0.83 to 1.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na: 0.25 to 2.62</td>
<td></td>
</tr>
</tbody>
</table>

able to ion pair with the same carbonyl anion, the two quaternary ammonium groups must be positioned close to each other.

The stability of (2) and (3) as judged by any change in the carbonyl region of the IR spectra is no different from what was reported for other very similar resin supported species. When stored under CO the IR spectra remain unaltered for several hours. We had also reported earlier that the catalytic activity of similar resin supported species increases substantially when they are subjected to mild thermal activation. This is expected since supported (1) is coordinatively saturated and mild thermal activation is necessary to remove all the CO groups. The same protocol has also been followed with (2) and (3). In other words all catalytic experiments with (2) and (3) have been carried out after heating them under vacuum until the bands due to \( \nu_{CO} \) disappear completely (see Experimental). The earlier reported species were found to undergo reversible decarbonylation. This aspect has not been studied in the present work.

Table 1 also contains surface area and pore size distribution data of (2) and (3). In terms of porosity (2) and (3) are noticeably different. In (2) majority of the pores fall within a narrow range while in (3) the pore size distribution is wider. In (2) pores having diameter between 5 to 60 Å occupy ~90% relative volume and the remaining ~10% is from macropores having diameter between 1900 to 2000 Å. In (3) pores having diameter between 5 to 80 Å occupy ~85% relative volume and the remaining ~15% is from macropores having diameter between 1900 to 2000 Å. In both the samples pores having diameter between 10 to 20 Å are the largest class interval, but in (2) and (3) they account for 33 and 19% of the relative volumes. The surface area of (3) is twice that of (2).

From SEM studies the shape, morphology and dimensions of the polymer particles in (2) and (3) are found to be similar but not identical. Representative micrographs are given in Fig. 2. For a given catalyst, the surface platinum concentrations of several particles at a number of different locations have also been measured by EDAX. From the average of such measurements the ranges of surface platinum concentrations of (2) and (3) have been calculated (see Table 1). For meaningful comparison the range is defined after normalizing the average surface platinum concentration to unity for both the samples. It is important to note that for (2) in agreement with atomic absorption analysis the presence of sodium is not seen by EDAX, but for (3), the presence of sodium is clearly detected.

(B) Catalytic hydrogenation-activity and selectivity

Samples (2) and (3) have been tested as catalysts for the hydrogenation of nitrobenzene, the ketonic functionality of \( \alpha- \) and \( \beta- \) ketoesters, and unfunctionalized ketones. The conversion, activity and selectivity data are given in Table 2.

It is apparent that for nitrobenzene and methyl pyruvate hydrogenation, the turnover numbers of both (2) and (3) are high and comparable. Both the catalysts are notably less active for all the other substrates. Thus for cyclohexanone and ethylacetacetate hydrogenation the turnover numbers are approximately two and one orders of magnitude less than that for methyl pyruvate or nitrobenzene respectively. Similarly for acetophenone hydro-
Table 2—Catalytic data

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product(s)</th>
<th>Catalyst</th>
<th>Conversion(%)</th>
<th>TON (× 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene</td>
<td>Aniline (2)</td>
<td>100; 2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylpyruvate</td>
<td>Methyl lactate (2)</td>
<td>100; 2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylacetocetate</td>
<td>Ethyl-3-hydroxy butyrate (2)</td>
<td>93; 2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>Cyclohexanol (2)</td>
<td>10; 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetophenone</td>
<td>1-Phenylethanol (2)</td>
<td>19.4; 0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All hydrogenation reactions were carried out with 1 millimole substrate and 30 mg catalyst. TON = millimole of product divided by millimole of Pt₁₅. 

15 bar hydrogen, 2 ml methanol, 12 h, 300K.
40 bar hydrogen, 1 ml methanol, 12 h, 300K.

Fig. 2.—SEM micrographs of (a) (2) and (b) (3).

Fig. 3.—Rate of hydrogenation of methylpyruvate by (2) (■) and (3) (●) under 15 bar H₂ pressure at 300K.

Hydrogenation the corresponding turnover numbers differ by approximately five times.

The activity of (2) as judged by turnover numbers is a little more than that of (3) for all the substrates except for cyclohexanone. However, for cyclohexanone both (2) and (3) show such low activity that the difference for this particular substrate may be ignored. The superior activity of (2) is apparent when the time monitored conversion values of the two catalysts are compared. Time versus conversion plots for methylpyruvate using (2) and (3) as catalysts are shown in Fig. 3. It is clear that the rate of conversion is higher with (2).

Although the total platinum content, surface platinum concentration as measured by EDAX, and the surface area of (3) are more than that of (2), the latter is catalytically slightly more active. One of the plausible reasons for the higher activity of (2) is probably the absence of sodium on its surface. As mentioned earlier EDAX analysis shows that sodium is present on the surface on an average to about 20% of the concentration of platinum. The following two conclusions may be drawn from this.

First, sodium must be present as the counterion of (1). For a given (1) where sodium is present as a cation, we are not in a position to say if both the counter ions are sodium, or one is sodium and the other is a quaternary ammonium group. Second, if both the counter ions are sodium then the sodium salt of (1) must be trapped inside the pores of the polymer and is not removed even by repeated washing with methanol. In either case the catalytic sites, derived
from sodium associated (1), are proposed to be less active. As a follow up to our earlier reports where 20% DVB cross-linked chloromethylated polystyrene was used, the 5.5 and 8% cross-linked polymers have also been functionalized with chiral cinchonine rather than triethylamine. After exchanging the chloride anions of the resultant materials with (1), they have been tested as potential asymmetric hydrogenation catalysts for methyl pyruvate. Surprisingly unlike with the 20% cross-linked catalyst where ~80% enantioselectivity was observed, no enantioselectivity is observed with (2) or (3). It is to be noted that the main difference between the 20% cross-linked polystyrene on the one hand, and 5 and 8% materials on the other, is their degree of chloromethylation. All the three chloromethylated samples are commercially purchased ones from different suppliers, and the degree of chloromethylation in the 20% sample is about four times less compared to the other two. A detailed explanation of how the degree of chloromethylation is related to the observed difference in enantioselectivity will be reported in another publication.

Acknowledgement

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References