

Platinum carbonyl derived catalysts on inorganic and organic supports: a comparative study

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Abstract

Fumed silica, silica gel, silica–alumina and cross-linked (5.5%) polystyrene have been functionalized with quaternary ammonium groups and the Chini cluster $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ has been anchored onto these functionalized materials by ion pairing. A catalyst has also been prepared by the adsorption of $\text{Na}_2[\text{Pt}_{12}(\text{CO})_{24}]$ on unfunctionalized fumed silica. The catalytic activities of the resultant materials, and that of commercially purchased 5% platinum on alumina have been studied for the hydrogenation of a variety of unsaturated compounds. The substrates studied are: α -acetamidocinnamic acid, cyclohexanone, acetophenone, methyl pyruvate, ethyl acetoacetate, nitrobenzene and benzonitrile. Compared to the polystyrene supported catalyst, the inorganic oxide supported catalysts have higher surface areas and for most of the substrates have notably higher activities. The functionalized fumed silica-based catalyst gives higher conversions than functionalized silica gel and silica–alumina-based catalysts. In the hydrogenation of acetophenone and ethyl acetoacetate, the functionalized fumed silica-based catalyst show superior activity compared to the commercial platinum catalyst, and the catalyst made by conventional adsorption method. In benzonitrile hydrogenation with all the cluster-derived catalysts a hydrazine derivative is selectively formed, but when the commercial platinum catalyst is used benzyl amine is the main product.

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1. Introduction

Anchoring of homogeneous catalysts onto insoluble polymeric supports has been much investigated for achieving a simple and easy method for the separation of the catalyst [1]. Supported carbonyl clusters in addition have the potential to generate small metal crystallites of novel catalytic properties [2]. Because of these two reasons catalysts made by supporting carbonyl clusters on inorganic or organic polymeric materials continues to be an area of active research [1,2]. While considerable progress has been made elucidating structural details of cluster derived particles, the practical

advantages of such an approach for making catalysts remain to be firmly established.

The physico-chemical properties of the Chini clusters, $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 3, 4, 5$), have been much studied and we have reviewed and reported their use both as supported and as homogeneous catalysts [3a,3b,3c]. We had also reported the use of commercial anion exchange resin as a support material for a number of anionic carbonyl clusters, including the Chini clusters, many years ago [3d]. Later on this method of *ion-pairing* Chini clusters on suitable *organic supports* was found to be of special interest because of the ability of the resultant materials to catalyze hydrogen driven reductions of redox active biomolecules, and asymmetric hydrogenation of methyl pyruvate [4–6]. Very recently we communicated the catalytic performance of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ (**1**), ion-paired on functionalized fumed silica, in hydrogenation reactions [7].

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The work reported here has been carried out with following objectives. First, to compare the performance of the catalyst made by ion-pairing (**1**) on functionalized silica on the one hand, and functionalized divinyl benzene cross-linked polystyrene on the other. Although we have recently reported the effect of cross-linking on the catalytic performance, studies that compare the relative performance of organic vs. inorganic supports have not been reported [8]. Second within the family of functionalized inorganic supports, we wanted to see the effect of changing the support on catalytic performance. Importantly, the results show that (**1**) anchored on functionalized fumed silica gives a superior catalyst than commercial platinum on alumina, and also a catalyst made by simple adsorption of the cluster on unfunctionalized fumed silica.

2. Results and discussion

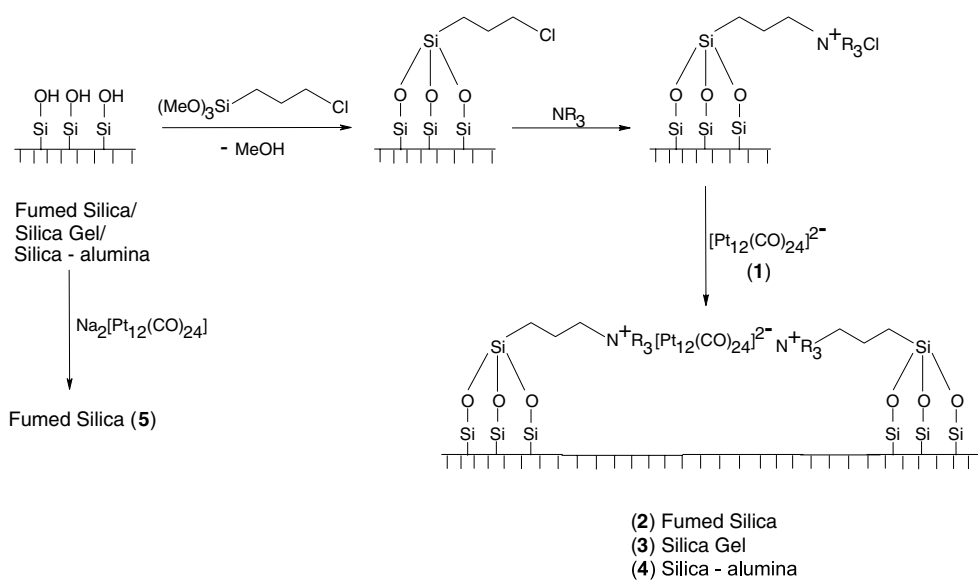
2.1. Preparation and characterization of the precatalysts

In the work presented here fumed silica, silica gel, silica–alumina and commercially available chloromethylated 5.5% divinyl benzene cross-linked polystyrene have been used as the inorganic and organic support, respectively. Commercially available platinum on alumina has also been used for comparative performance evaluation with the cluster-derived catalysts. As reported earlier, the chloromethylated resin may be reacted with triethyl amine to give quaternary ammonium functionality. The silica-based inorganic supports require prior treatment with trimethoxychloropropyl silane (Scheme 1). The chloride anions of the

resultant materials may then be exchanged with (**1**). This is effected by a treatment of the functionalized support with a methanolic solution of the sodium salt of (**1**). Repeated washing of the resultant material with methanol removes all physically adsorbed sodium salt of (**1**).

The designation of the supported materials with the degree of functionalization determined from analytical data is given in Scheme 1 and Table 1. While samples (**2**), (**3**), (**4**) and (**7**) have been prepared by functionalization of the supports followed by anion exchange, sample (**5**) has been prepared by conventional adsorption method with *unfunctionalized* fumed silica as the support. To obtain meaningful comparative data on catalytic performance (see later), the amount of platinum loading in (**5**) has been maintained nearly at the same level as that of (**2**).

Evidence for the successful incorporation of functional groups in the silica network comes from analytical and spectroscopic (Si^{29} NMR (MAS), IR and UV–Vis) data. The CPMAS spectra of silica before and after treatment with $(\text{OMe})_3\text{Si}(\text{CH}_2)_3\text{Cl}$ have been reported in the literature [9]. Representative Si^{29} NMR (MAS) spectra obtained from samples used in this work are shown in Fig. 1. The chemical shifts of signals in Fig. 1(a) and (b) agree well with the literature reported values of $(-\text{O}-)_4\text{Si}$, $(-\text{O}-)_3\text{Si}-\text{OH}$, $(-\text{O}-)_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ and $(-\text{O}-)_2\text{Si}(\text{OMe})(\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl})$. Further functionalization by treatment with NEt_3 causes the signals due to Si atoms with Si–C bonds to be broadened. This broadening is presumably due to the coupling of silicon nuclei with quadrupolar $\text{N}^{14}(I = 1)$. On incorporation of (**1**) by anion exchange, all the signals are merged and only one broad signal is observed. It is

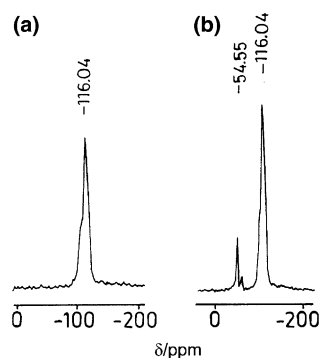


Scheme 1. Functionalization of the supports and synthesis of the supported cluster-based precatalysts. Catalyst (**7**) = (**1**) supported on 5.5% divinyl benzene cross-linked polystyrene through ion pairing.

Table 1

Designations, functionalization and platinum content of supported clusters and commercial catalyst

Support	Designation	Functionalization ^a (%)			Total Platinum ^b (wt%)
		“Chloro” functionality	NEt ₃	Pt ₁₂ (CO) ₂₄ ²⁻	
Fumed silica	(2)	54	7	0.12	2.8
Silica gel	(3)	14	5	0.04	1.5
Silica–alumina	(4)	21	5	0.05	1.4
Fumed silica without functionalization	(5)	None. Prepared by conventional adsorption method	None	None	2.7
Alumina	(6)	None. Commercial sample	None	None	5
Cross-linked (5.5%) chloromethylated polystyrene	(7)	87	65	0.3	3.8

^a Degree of functionalization calculated on the basis of analytical (C, H, N, Pt) data.^b By atomic absorption.Fig. 1. Si²⁹ NMR (MAS) of (a) fumed silica and (b) fumed silica after treatment with trimethoxychloropropyl silane.

reasonable to assume that this is due to further coupling of the silicon nuclei with Pt¹⁹⁵ ($I = 1/2$).

Evidence of initial retention of molecular identities by (1) on all the supports comes from the characteristic IR and UV–Vis. spectrophotometric signatures of the carbonyl anions [7]. Barring (5) and (6), all the other samples when freshly prepared have IR signals and

UV–Vis. bands that match well with those of [Pt₁₂(CO)₂₄]²⁻ ($\nu_{\text{CO}} \sim 2040$ and 1860 cm^{-1} , strong charge transfer UV–Vis band at $\sim 620 \text{ nm}$). However, the nature of the support has a major effect on the stability of the supported cluster. Thus for (2), (3) and (4) even when they are stored under CO, the characteristic IR and UV–Vis. bands of (1) disappear quickly. In contrast under identical conditions, in (7) the spectral signatures of (1) remain intact for more than 24 h. In sample (5), the IR or UV–Vis. bands of (1) are not seen even with a freshly prepared sample. IR spectra of (2), (3) and (4) also show $\nu_{\text{C-H}}$ and $\nu_{\text{O-H}}$ bands providing additional evidence for incorporation of functional groups, and indicating retention of some hydroxyl functionalities (see later). Representative spectra are shown in Fig. 2.

The loss of the spectral signatures of (1) from (2), (3) and (4) is especially rapid if the protocol of drying the inorganic oxide (Section 4) is not strictly adhered to. As mentioned earlier, from the IR spectra it is apparent that fumed silica even after drying and functionalization has some unreacted hydroxyl functionalities and is hygroscopic (Fig. 2). As (1) is known to react with H⁺,

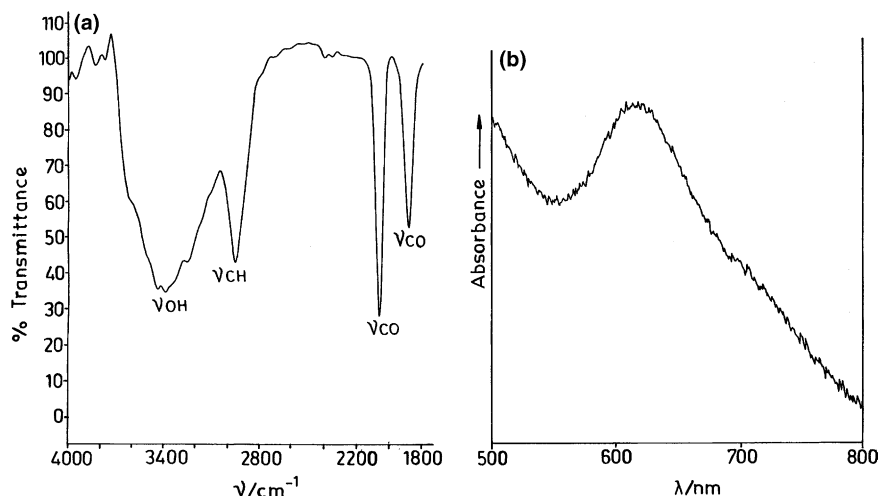


Fig. 2. (a) IR (KBr disc) and (b) UV–Vis spectrum (reflectance) of freshly prepared (2).

OH⁻, and water, the greater stability of (1) in (7) may partly be due to the hydrophobic environment of the polystyrene matrix.

Sodium analyses in (2), (3), (4), (5) and (7) have been carried out by both EDAX and atomic absorption. Repeated analyses either by atomic absorption or by EDAX do not show the presence of detectable amounts of sodium in (2), (3), (4) and (7). In contrast sodium is detected in (5). As shown in Scheme 1, in the proposed formulations of (2), (3), (4) and (7), 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 support with the sodium salt of (1). The absence of sodium implies that for these species, alternative formulations in which one cation is the quaternary ammonium group and the other is a sodium ion, if present at all, would be negligible in concentration. This however is not the case for (5). Since no ion exchange is involved in its synthesis, the presence of sodium is expected in (5), and is found to be present in about 1–3% of the concentration of platinum.

Analytical data (C, H, N and Pt) of (2), (3), (4) and (7) at different stages of preparation of the supported species have been measured and used for determining the degree of functionalization. The degree of functionalization is given in Table 1 and may be interpreted as follows. In (2) out of a thousand “SiO₂” units approximately 540 are functionalized by trimethoxychloropropyl silane. Out of these 540 units about 70 are quaternized by triethylamine, and only two out of these 70 take part in ion pairing with (1). The degree of functionalization is notably less when the support is changed from fumed silica to silica gel or silica–alumina. Thus in (3) and (4) out of a thousand “SiO₂” approximately 140 and 210 units, respectively are functionalized by trimethoxychloropropyl silane.

The analytical data of (7) indicate a somewhat different picture. On chloromethylation about 870 units are functionalized, and on treatment with NEt₃ out of this 870 units 650 units are quaternized. However, for all the supports, inorganic or organic, very few of the quaternary ammonium groups, are accessible for ion pairing

with (1). This may be due to the fact that to be able to ion pair with the same anionic cluster molecule, the two quaternary ammonium groups must be positioned close to each other.

Surface area, porosity and normalized platinum concentration on the surface, as measured by EDAX, of samples (2), (5) and (7) are given in Table 2. Compared to (2) the degree of functionalization and platinum loading in (3) and (4) are much less. Also, in catalytic experiments (see later), (3) and (4) give lower conversions than (2). For these reasons these measurements were not carried out for (3) and (4). In terms of porosity functionalized fumed silica-based catalyst (2), and unfunctionalized fumed silica-based catalyst (5) are very similar. However, on functionalization the surface area of fumed silica decreases by about 40%. The specific surface area of functionalized polystyrene-based catalyst (7) is more than an order of magnitude less than that of (2) and (5). In terms of porosity also (7) is notably different from (2) and (5). While in the silica-based catalysts about 30% of the pores are within the range of 80–100 Å, (7) does not have pores in this range and has considerably more small pores.

For a given catalyst, the surface platinum concentrations of several particles at a number of different locations have been measured by EDAX. From such measurements the ranges of *surface* platinum concentrations of (2), (7) and (5) have been calculated. For meaningful comparison the range is defined after normalizing the average surface platinum concentration to unity for each sample.

2.2. Catalytic hydrogenation-activity, selectivity and recycle

Samples (2)–(7) have been tested as catalysts for the hydrogenation of nitrobenzene, the ketonic functionality of α - and β -ketoesters, unfunctionalized ketones, benzonitrile and the olefinic double bond in α -acetamidocinnamic acid. The conversion, activity and selectivity data are given in Table 3. We had reported earlier that the catalytic activity of anion exchanger supported (1) increases substantially if it is subjected to mild thermal activation [3d]. This is expected since supported (1) is co-ordinatively saturated and mild thermal activation is

Table 2
Porosity, EDAX and surface area of (2), (5) and (7)

Catalyst	Relative volume (%) [pore ranges (Å)] ^a			Platinum concentration Normalized range on surface (EDAX data ^b)	Surface area ^a (m ² /gm)
	Large (>500)	Medium (80–100)	Small		
(2)	17	30	53 (20–70)	0.82–1.31	180
(7)	10	Nil	90 (10–60)	0.68–1.24	12
(5)	15	34	51 (20–70)	0.57–1.67	320

^a Measured by BET.

^b The range is given after normalizing the average for a given sample to 1.

Table 3
Conversion (%) data on hydrogenation of unsaturated substrates using (2) to (7) as catalysts^a

Substrate (product)	Catalyst					
	(2)	(3)	(4)	(5)	(6)	(7)
Nitrobenzene ^b (aniline)	100	100	100	100	100	100
Methyl pyruvate ^c (methyl lactate)	100	100	100	100	100	100
Ethyl acetoacetate ^c (ethyl-3-hydroxybutyrate)	100	85	77	76	26	9.5
Acetophenone ^c (1-phenylethanol)	100	57	87	62	40	19
Cyclohexanone ^c (cyclohexanol)	69	56	60	56	24	2
α -Acetamidocinnamic acid ^d (<i>rac</i> - <i>N</i> -acetylphenylalanine)	96	58	70	73	79	5
Benzonitile ^e (Benzylamine, <i>N,N</i> -dibenzylhydrazine)	100 (10,90)	80 (12,68)	86 (8,78)	99 (7,82)	40 (40,0)	45 (4,41)

^a All hydrogenation reactions were carried out with 1 millimole substrate and 30 mg catalyst.

^b 15 bar hydrogen, 2 ml methanol, 12 h, 300 K.

^c 40 bar hydrogen, 1 ml methanol, 12 h, 300 K.

^d 40 bar hydrogen, 2 ml methanol, 12 h, 300 K.

^e 15 bar hydrogen, 1 ml methanol, 24 h, 373 K.

necessary to remove all the CO groups. Indeed IR monitoring had clearly established that thermal activation causes complete disappearance of ν_{CO} . In contrast, as already mentioned (2), (3) and (4) and (5) undergo rapid CO loss, and do not require thermal treatment for decarbonylation. However, to maintain a uniform protocol, all catalytic experiments with (2)–(7) have been carried out after subjecting them to mild thermal activation (Section 4). The structures of the catalytic sites after decarbonylation and in the thermal activated materials have not been investigated.

For nitrobenzene and methyl pyruvate hydrogenation, all the catalysts give full conversions. This however is not the case for the other substrates where the inorganic oxide supported catalysts show higher activities than the polystyrene-based one. Thus for α -acetamidocinnamic acid, cyclohexanone, ethylacetoacetate and acetophenone hydrogenation, the conversions obtained with (2)–(5) are about 60–100% while with (7) they are ~2–20%. The overall higher activities of (2)–(5) than that of (7) must partly be due to the higher surface areas of the former class of catalysts. As mentioned earlier, among (2), (3) and (4), (2) gives higher conversions than the other two for all the substrates. For this reason as a representative of functionalized inorganic oxide-based catalyst, (2) has been used in all the comparative rate studies (see later).

To find out if the specially prepared cluster derived catalyst (2) offers any practical advantages over the commercially available platinum catalyst (6), or the catalyst prepared by simple adsorption i.e., (5), their activities may be compared. The commercial platinum catalyst (6) chosen for this purpose was 5% platinum on alumina (Aldrich 2000–01, Catalogue No. 31,132–4). As can be seen from Table 3, the conversions obtained with (2) in most cases are more than those with (5) or (6). The superior activity of (2) becomes evident when the time monitored conversion values of all the catalysts are compared. Time versus conversion plots for acetophe-

none and ethyl acetoacetate using (2), (5), (6) and (7) are shown in Fig. 3.

It is clear that for both the substrates the rates of conversion are in the order (2) > (5) > (6) > (7). With (2) the rate of hydrogenation of acetophenone is about three, five and 16 times that of (5), (6), and (7), respectively. For the hydrogenation of ethylacetoacetate it is about two and a half, seven, and 30 times that of (5), (6)

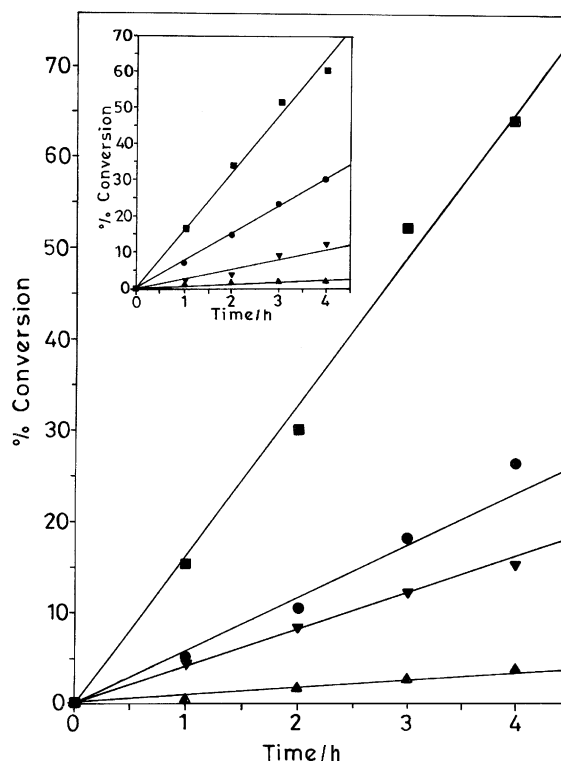


Fig. 3. Rate of hydrogenation of acetophenone by (2) (functionalized fumed silica) (■), (5) (physical adsorption on fumed silica) (●), (6) (commercial catalyst) (▼) and (7) (functionalized polystyrene) (▲) under 40 bar hydrogen pressure at 300 K. Inset shows the rate of hydrogenation of ethylacetoacetate. Least square fitted straight lines are drawn to highlight the differences in apparent rates.

and (7). It may be noted that while the variation in surface platinum distribution of (2) and (7) are similar, total platinum content of (7) in fact is about 30% more than that of (2) (Tables 1 and 2). The significantly higher activity of (2) compared to that of (7) is therefore must be due to its much higher surface area.

In view of the fact that the surface area of (5) is considerably more than that of (2), the higher activity of the latter is surprising. As mentioned earlier the total platinum contents of (2) and (5) are nearly the same, differing only by about 3%. The observed difference in activities is therefore not a result of difference in the total platinum content.

Chemical functionalization is known to bring about a noticeable change in the morphology of the support. Thus by TEM several nanotubes of about 200 nm diameter have been observed in (2) but in (5) no such regular shapes could be found [7]. This suggests that chemical functionalization followed by ion pairing takes place on the relatively more exposed and easily accessible surface sites. This is expected to result in a more uniform platinum distribution on the surface than what may be achieved by the adsorption method. In the adsorption method some of the clusters are expected to diffuse deep inside the matrix and stay buried.

This explanation is consistent with the EDAX data (Table 2). Although the total platinum contents of (2) and (5) are almost identical, the variation in the surface platinum concentration of (5) is significantly more than that of (2). As mentioned earlier EDAX analysis of (5) also shows that sodium is present on the surface on an average to about 1–3% of the concentration of platinum. This suggests that the catalytic sites, derived from sodium associated (1), are probably less accessible to the reactants and less active.

As the main reason for surface anchoring of (1) through ion pairing is to generate a catalyst that may be recycled, successive hydrogenation reactions using recycled (2) have been performed. The hydrogenation of methyl pyruvate using recycled (2) has been carried out 10 times and no drop in activity is observed. This suggests that in the catalyst prepared by the ion pairing method, the active sites are sufficiently strongly bound so as to resist leaching under the experimental conditions.

Finally in nitrile hydrogenation reactions, the selectivities of the *cluster derived* catalysts (2)–(5) on the one hand, and the commercial catalyst (6) on the other, may be compared. There are many reports in literature on the hydrogenation of benzonitrile and the relevant mechanistic aspects [10]. With conventional heterogeneous catalyst benzyl amine is the main product but formation of secondary and tertiary amines are also known. With the commercial catalyst (6), total conversion of benzonitrile with selectivity towards benzyl amine >95% is observed. Surprisingly under identical

conditions with all the cluster-based catalysts, a hydrazine derivative $\text{Ph-CH}_2\text{-NH-NH-CH}_2\text{-Ph}$, characterized by NMR and mass-spectrometry, is the main product.

With these catalysts the selectivity towards $\text{Ph-CH}_2\text{-NH-NH-CH}_2\text{-Ph}$ lies within 80–90%. By using butyronitrile as an additional nitrile substrate, the generality of this reaction has been established. With (2) and (5) as the catalysts 100% conversions with more than 90% selectivity to $\text{C}_4\text{H}_9\text{-CH}_2\text{-NH-NH-CH}_2\text{-C}_4\text{H}_9$ are obtained. In contrast, with (6) as the catalyst total conversion of butyronitrile exclusively to amylamine is observed.

There are many cluster complexes where structure determination by single crystal X-ray shows that the “C–N” moiety interacts with more than one metal atom [11]. Since high selectivity towards hydrazine derivatives is observed with all the cluster derived catalysts, it is possible that similar mechanism operates for all of them, and one of the steps involved is a multimetal activation of the “C–N” moiety as has been observed for discrete cluster complexes. However to the best of our knowledge in cluster organometallic chemistry there is no example of the coupling of two “C–N” units through N–N bond formation. The selective formation of hydrazine derivatives as reported in this work must involve such a coupling reaction.

3. Conclusion

Ion pairing of Chini clusters on functionalized silica is found to be a viable method for making a novel hydrogenation catalyst. Such a catalyst is found to be more active than the catalyst obtained by simple adsorption of the cluster on the support. While the precise structures of active sites in these catalysts are not known, the activities of *both* the cluster-derived catalysts are found to be more than that of a commercial platinum catalyst. In benzonitrile hydrogenation unlike the commercial catalyst that gives exclusively benzylamine, the cluster-derived catalysts give hydrazine derivatives.

4. Experimental

Chloroplatinic acid was purchased from Johnson Mathey, London. 5.5% Merifield polystyrene, methyl pyruvate, methyl lactate, benzylamine and α -acetamidocinnamic acid were purchased from Fluka, Switzerland. Fumed silica, silica–alumina (Aldrich’2000–01; 31,132–4), 1-phenylethanol, ethyl-3-hydroxy butyrate and 5% platinum on alumina were obtained from Aldrich, USA. Silica gel (S.D. Fine Chemicals, India, mesh 60–120), nitrobenzene, anilines, cyclohexanone,

cyclohexanol, benzonitrile, ethylacetoacetate, acetophenone, triethylamine and other organic solvents used in this work were procured from S.D. Fine Chemicals, India.

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 $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ was synthesized according to the literature reported procedure [12]. Hydrogenation experiments were carried out in an autoclave. Hydrogenation of all substrates except α -acetamidocinnamic acid and nitriles were monitored by gas chromatography (GC) using a SC-30 (mesh 1000–2000) GC column with FID detector. Hydrogenation of α -acetamidocinnamic acid was monitored by $^1\text{H-NMR}$ and that of benzonitrile and butyronitrile was monitored by GC–MS. All hydrogenated products except, *N,N*-dibenzylhydrazine were initially identified by using authentic commercial samples of the expected products. *N,N*-Dibenzylhydrazine was identified by mass spectrometry and $^1\text{H-NMR}$. Porosity and surface area measurements were carried out on a BET surface area analyzer. Solid state NMR (Si^{29} MAS) spectra were recorded using 300 MHz FT-NMR spectrometer. IR spectra were taken on a Nicolet Impact 400 spectrophotometer. Reflectance spectra were measured using a Shimadzu UV-260 spectrophotometer. SEM (EDAX) measurements were carried out with a 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.

4.1. Functionalization of fumed silica

Fumed silica was dried at 200 °C under vacuum for 24 h. Dried fumed silica (1 g) was treated with neat 3-chloropropyltrimethoxy silane (15 ml) at 160 °C in oil bath for 96 h. It was then filtered and washed thoroughly using toluene followed by methanol. On functionalization initial white color of the solid support changed to pale yellow. The same procedure was followed for the functionalization of silica–alumina and silica gel.

4.2. Modification of the functionalized fumed silica by triethylamine

The chloropropylsilane functionalized fumed silica (1 g) was mixed with 10 ml triethylamine and 10 ml toluene. The mixture was heated at reflux for 96 h. It was then filtered and washed thoroughly with toluene followed by methanol. The same procedure was followed for the functionalization of silica–alumina and silica gel. The modification of the 5.5% chloromethylated cross-

linked polystyrene by triethylamine was carried out in a similar fashion.

4.3. Synthesis of (2)

To a deep blue solution of $\text{Na}_2[\text{Pt}_{12}(\text{CO})_{24}]$ (200 mg) in 15 ml methanol, the triethylamine modified functionalized fumed silica (1 g) was added and the mixture was stirred for 96 h under carbon monoxide atmosphere at room temperature (300 K). The solid material was filtered off and washed repeatedly with methanol and dried under a flow of CO. Synthesis of (3), (4) and (7) were carried out in a similar fashion except for (7) only 12 h were required for ion exchange.

4.4. Synthesis of (5)

To a deep blue solution of $\text{Na}_2[\text{Pt}_{12}(\text{CO})_{24}]$ (200 mg) in 15 ml methanol, fumed silica (1 g) was added and the mixture was stirred for 96 h under carbon monoxide atmosphere at room temperature (300 K). The solid material was filtered off and washed repeatedly with methanol and dried under a flow of CO.

4.5. Thermal activation of (7)

The supported material (7) (1 g) was taken in a three necked round bottomed flask (25 ml) equipped with nitrogen and vacuum adapter and was flushed with nitrogen to remove any residual oxygen. The system was then evacuated under vacuum at 343 K for one hour and the color of the beads changed from green to gray. The system was then cooled to room temperature and the activated material stored under nitrogen. The IR spectrum of the activated material showed complete absence of inorganic carbonyl bands. It was used for hydrogenation reactions within one hour of its synthesis. (2)–(6) were subjected to the same treatment before using them as catalysts.

4.6. Catalytic experiments with (2)

All hydrogenation reactions were carried out with 1 mmol of the organic substrate and 30 mg of (2) in methanol. The hydrogen pressure, temperature, reaction time, and amount of methanol used for different substrates are given in Table 3. At the end of the catalytic run the reaction mixture was subjected to GC or GC–MS (for the hydrogenation of benzonitrile and butyronitrile) and extent of conversion was calculated on the basis of the area ratios of starting material and product. Catalytic experiments with (3) to (7) were carried out in a similar fashion. For the time-monitored conversion data the amounts of (2), (5), (6) and (7) used were adjusted in such a way that the total platinum content in each case was identical.

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