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Designed precursor for the controlled synthesis of highly active atomic and sub-nanometric platinum catalysts on mesoporous silica

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Abstract: Development of new methods to synthesize nanometric metal catalysts has always been an important and prerequisite step in advanced catalysis. Herein, we design a stable nitrogen ligated Pt complex for the straightforward synthesis by carbonization of uniformly sized atomic and subnanometric Pt catalysts supported on mesoporous silica. During the carbonization of the Pt precursor into active Pt species, the nitrogen containing ligand directed the decomposition in a controlled fashion to maintain uniform size of the Pt species. The nitrogen ligand showed key role to stabilize the single Pt atoms on a weak anchoring support like silica. The Pt catalysts exhibited remarkable activities in the hydrogenation of common organic functional groups with turnover frequencies higher than in previous studies. By a simple post-synthetic treatment, we could selectively remove the Pt nanoparticles to obtain a mixture of single atoms and nanoclusters, extending the applicability of the present method.

Introduction

Precise control of active catalytic sites plays a crucial role in designing highly effective heterogeneous catalytic systems. In particular, the size of the metal species, such as single-sites, metal nanoparticles (NPs), or bulk state, directly affects their catalytic activities.^[1] Development of synthetic strategies that can control the nature of the active catalytic centres, switching from single-sites to nanostructure ensembles, is therefore both an important and yet challenging task. Conventional methods, such as sol-gel and wet impregnation, are widely accepted due to their inherent simplicity in employing simple metal salt precursors, such as nitrates, chlorides, and acetates. However, these methods do not normally provide satisfactory control over particle size. It is often observed that the thermal treatment during syntheses or catalytic processes induce aggregation of the active species to form large NPs (>5 nm), resulting in a decrease of

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catalytic activity.^[2] A plausible way to address this problem is the employment of stable metal complexes as the catalyst precursor, since these compounds have higher thermal stabilities than those of simple metal salts, and would gradually decompose upon increasing the temperature, allowing uniform formation of small metal NPs. Indeed, several organometallic complexes with unique properties have been employed as metal precursors to form structured metal NPs with controlled size.^[3] Mononuclear organometallic complexes have also been demonstrated as promising precursors to produce catalytic active sites as metal clusters.^[4]

Nitrogen ligand containing transition metal (e.g. Fe, Co, Ni) complexes were recently employed as precursors that could effectively produce single atom active sites after pyrolysis over suitable supports.^[5] In all cases, the M–N–C (M typically refers to transition metals) structure was retained in the catalysts due to the strong M–N bond. As a result, high metal loading (up to 4 wt%) could be obtained without considerable agglomeration of single active sites. Similarly, metal organic framework (MOF) approach was applied to synthesize single site catalysts, where carbonization at high temperature produced porous N-doped carbon support with anchoring groups to stabilize the metal atoms.^[6] It was proven that the M–N–C catalysts had comparative electrochemical performances with that of commercial Pt/C catalyst due to the presence of conductive $M-N_x$ coordination spheres. N-doped metal catalysts have also shown improved activities in different organic transformation. For example, Co-N-C system showed superior catalytic activity in coupling reactions due to electron-rich metal sites adjacent to the N atoms.^[5a] It was recently reported that the M-N species offered favourable adsorption of reactants on the active sites, facilitating product formation.^[7]

Several metal oxides including Fe₂O₃,^[8] Al₂O₃,^[9] CeO₂,^[10] TiO₂,^[11] $ZnO^{[12]}$ and nitrides such as $C_3N_4{}^{[13]}$ and $TiN^{[14]},$ as well as heteropoly acids^[15] have been used to stabilize single metal atoms and sub-nanoclusters due to the presence of anchoring sites or lattice defects. However, in spite of high surface area, it is still challenging to stabilize SACs and sub-nanoclusters on silica, presumably due to its weak metal-support interaction. Herein, we report a stable mononuclear Pt complex based on a pyridinebased tridentate ligand (tris(t-butyl)terpyridine or TBTP), which produced uniformly sized nanometric Pt species along with single Pt atoms over mesoporous SBA-15 silica. The bulky TBTP ligand is designed to protect the Pt species and provides high thermal stability due to the presence of strong Pt-N bonds. As a result, the decomposition of the Pt complex occurred in a well-controlled fashion to yield increased population of catalytically active single Pt atoms.

FULL PAPER

Results and Discussion

We followed a simple two-step procedure to synthesize the mononuclear Pt complex ([Pt(^tBu₃tpy)Cl]Cl or Pt(TBTP)) (see supporting information), and the product was characterized using ESI-MS analyses (Fig. 1(a)) which showed a strong molecular ion peak at m/z 632.2. Thermogravimetric analyses (Fig. 1(b)) revealed that the Pt complex was stable up to 350 °C before starting to decompose and the weight of the residue became stable from 450 °C onwards. Supported Pt catalysts (designated as xPt-SBA-15-T, where x is Pt loading and T is treatment temperature) with different metal loading were prepared by wet impregnation method. To obtain information on the formation of species, temperature programmed desorption-mass Pt spectrometry (TPD-MS), elemental analysis (EA) and X-ray photoelectron spectroscopy (XPS) studies were conducted with 1.5 wt% Pt(TBTP) complex supported on SBA-15. TPD-MS profile (Fig. 2) showed the loss of carbon species in the form of CO and CO₂ at different temperatures. Presumably, the silica support provided trace amount of oxygen for carbon oxidation. Up to 600 °C, significant amount of carbon was retained and a very little amount of nitrogen loss was observed. XPS results (Fig. S1) showed that the oxidation state of Pt remained the same as in the Pt precursor after treatment at 400 °C. For treatment temperature at 500 °C however, Pt species exhibited different oxidation states due to partial removal of ligand and formation of clusters/NPs. Nitrogen content also decreased upon increasing treatment temperature from 400 °C to 500 °C. In both samples, nitrogen species were observed in the form of imine bonding modes (C=N-C). Combination of TPD-MS, EA and XPS studies reveal that both carbon and nitrogen species were partly retained on the support, which stabilized the positively-charged Pt single atoms and close to zero-valent, small clusters (vide infra).



Figure 1. (a) ESI-MS spectrum and (b) TGA-DTA profile of $\mathsf{Pt}(\mathsf{TBTP})\mathsf{Cl}_2$ complex.

Initial characterization results showed that the heat treatment of supported Pt sample (0.2 wt% Pt) at 500 °C produces a mixture of single atoms and small clusters (or NPs) as observed from the IR spectra (Fig. 3(a)). Two characteristic peaks located at 2090 cm⁻¹ and 2075 cm⁻¹ can be assigned as linearly adsorbed CO on Pt single atoms and clusters (or NPs) respectively. XPS results also supported this observation since Pt moieties existed in partially oxidized state (Fig. S2(a)). When the temperature was increased to 600 °C, the IR peak at 2090 cm⁻¹ shifted to 2087 cm⁻¹ with concomitant peak-broadening, presumably due to the combination of the two peaks (Fig. 3(b)), indicating the higher

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heterogeneity of Pt species. The metallic character also increased at higher temperatures, which could possibly decrease the percentage of single atom species. However, NPs were hardly observed for any of these samples from TEM (Fig. 5(c) and S4(a, b)). When the loading was increased to 0.3 wt%, the IR peak at 2090 cm⁻¹ was totally abrogated and the peak at 2076 cm⁻¹ became broader and unsymmetrical (Fig. 3(c)), which indicated the presence of a mixture of clusters and NPs. When the metal loading was increased to 1.0 wt%, the IR peak at 2074 cm⁻¹ became much broader (Fig. 3(d)), indicative of NPs formation. Further evidence was provided by TEM analysis where NPs with an average diameter of ~3 nm were detected (Fig. S4(e, f)). XRD analysis of the sample showed a small peak at 39.7° (Fig. 5(a)) which was not clearly observed in other two samples at lower loading.



Figure 2. TPD-MS profile of Pt-complex supported on SBA-15.



Figure 3. IR spectra of CO adsorbed on different samples: (a) 0.2Pt-SBA-15-500, (b) 0.2Pt-SBA-15-600, (c) 0.3Pt-SBA-15-500, (d) 1.0Pt-SBA-15-500. Spectra were taken under N_2 flow after CO adsorption.

WILEY-VCH

FULL PAPER

To provide direct evidence on the local Pt coordination structure, X-ray absorption studies were performed. Extended X-ray absorption fine structure (EXAFS) spectra (Fig. 4(a)) revealed that both Pt-Pt and Pt-O(or N) contributions in the 0.2Pt-SBA-15-500 sample, indicative for significant Pt-Pt contribution. At decreased Pt loading (0.1 wt%), the sample showed higher amounts of Pt-O(or N) contribution. The weaker peak at 2.75 Å could correspond to the higher shell of Pt-O(or N) contribution as observed in the L₃-edge k-space spectra (Fig. S3).^[16] Fig. 2(b) showed the normalized X-ray absorption near-edge structure (XANES) spectra of the two samples, and the reference spectra of Pt foil and PtO2. The white-line intensities in the spectra reflected the positive oxidation state of Pt in two samples with different loading. The Pt species in 0.1Pt-SBA-15-500 sample carried higher positive charges, suggesting the dominance of Pt-O(or N) contribution. At higher loading the white-line intensity was closer to that of the Pt foil, which suggested that the sample contained Pt clusters or NPs.



Figure 4. (a) EXAFS and (b) XANES spectra of Pt-SBA-15 materials at two different Pt loading.

To validate the effectiveness of our present methodology, controlled catalysts (designated as xPt-SBA-15-T-C) using H₂PtCl₆ precursor were prepared using the same method. IR spectra of controlled catalysts at a loading of 0.3 and 1.0 wt% showed the characteristic peaks at 2063 and 2062 cm⁻¹ (Fig. S5(a and b)), designated as the linearly adsorbed CO on NPs. The controlled sample of 0.2 wt% Pt loading did not show any CO adsorption. XRD analysis revealed obvious peaks at 39.7°, 46.2° and 67.4° corresponding to the crystalline plane (111), (200) and (220) of Pt NPs for these samples (Fig. 5(b)).^[17] The peak intensities increased with Pt loading, implying increased particle sizes, which was further confirmed by TEM analysis (Fig. S4(g, h)). H₂ pulse titration experiment provided the dispersion of Pt over SBA-15 in both cases. Pt dispersion was observed to be much higher in the samples derived from Pt(TBTP) precursor compared to H₂PtCl₆ (Fig. S6).

The catalytic performance of the catalysts was tested in the hydrogenation of different functional groups. Catalysts prepared from the Pt(TBTP) complex showed very high activities as compared to the catalysts prepared from H_2PtCl_6 . Using a very low Pt/substrate ratio (1:4000), almost quantitative conversion could be achieved in the hydrogenation of phenylacetylene (Table S4). At longer reaction times, the catalysts treated at 500 °C gave higher selectivity for semi-hydrogenation product as compared to controlled catalysts. To obtain the intrinsic hydrogenation activities of the catalysts, CS_2 poison titration method was

adopted to determine the surface atom fraction (Fig. S7). Assuming that each CS₂ molecule blocked two surface Pt atoms, we determined the surface atom fraction to be 20% and 1.5% for 0.2Pt-SBA-15-500 and 0.2Pt-SBA-15-500-C catalysts, respectively, which was in accordance with the results obtained from H₂ pulse titration method.



Figure 5. XRD spectra of Pt-SBA-15 materials at different loading prepared from (a) TBTP complex and (b) H_2PtCl_6 precursors. TEM images of (c) 0.2Pt-SBA-15-500 and (d) 0.2Pt-SBA-15-500-C.

The activities of the catalysts were further verified for the hydrogenation of -NO2 group in nitrobenzene (Table S5). The main purpose of selecting the hydrogenation of -NO2 group is to differentiate the nature of Pt species based on the product selectivities. Since -NO2 group is very easy to be reduced; its hydrogenation depends on many factors including both catalyst features and reaction conditions. The hydrogenation of nitrobenzene follows sequential steps to give aniline as final product and produces different intermediates during the reaction. In a fixed reaction condition, the product selectivity is observed to be dependent on nature of the metal, oxidation state of the metal and acid-base property of the catalyst support. Since in the present case, we use only Pt metal as catalyst and the silica support is neutral, the product selectivity is expected to be dependent on the oxidation state of Pt species only. Very high reaction rates were observed for the Pt-SBA-15 catalysts compared to the controlled catalysts (Pt-SBA-15-C). Notably, the product distribution was drastically different. Over Pt-SBA-15 catalysts, four different products were detected, including aniline, nitrosobenzene, azobenzene, and azoxybenzene with aniline as the major product (Table S5). In sharp contrast, aniline was the only product obtained over Pt-SBA-15-C. This could be attributed to the presence of both positively charged single atoms as well as reduced NPs in Pt-SBA-15 which gave different intermediate products along with targeted aniline. In case of the catalyst (A) derived from Pt(TBTP) precursor, the Pt species are slightly oxidized due to the presence of single atoms and nanoclusters, and therefore produced significant amount of intermediate products (such as nitrosobenzene and azoxybenzene in this

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FULL PAPER

case). However in case of controlled catalyst (A-C), the Pt species are highly reduced due to the formation of nanoparticles, and therefore gave the fully hydrogenation product, i.e. aniline. We also compared the turnover frequency (TOF) of our catalysts with previously reported nanometric and single atom Pt catalysts for the hydrogenation of $-C\equiv C$, $-NO_2$ and -C=O groups (Table 1 and 2). Several-fold increments of activities were observed as compared to the previously reported Pt catalysts. In particular, the TOFs for $-NO_2$ hydrogenation were exceptionally high, which was presumably due to the presence of Pt–N species, favouring the dissociative adsorption of the reactant nitrobenzene and facilitated the desorption of the product aniline.^[7]

After studying the hydrogenation of $-C \equiv C$ and $-NO_2$ functionalities, we sought to find out the activities of our catalysts in -C=O bond hydrogenation. The experiments were carried out at high stirring speed to rule out mass transfer limitations (see Fig. S8 for the effect of stirring speed). Effects of different parameters (reaction time, temperature and H₂ pressure) were studied (Fig. S9, S10, S11), which reveal that Pt-SBA-15 performed considerably better than Pt-SBA-15-C. Kinetic studies were also performed (Fig. S12). Both catalysts followed first order kinetics up to a certain concentration of benzaldehyde in presence of a fixed amount of catalyst. However, the reaction rate of Pt-SBA-15 was much higher than the Pt-SBA-15-C in all experiments. The reusability of the catalyst was examined in the hydrogenation of benzaldehyde at an optimized condition; the activity was retained for up to seven consecutive cycles (Fig. S13).

Based on the earlier studies made on gold and iron,^[23] we propose that the Pt NPs in the catalyst could be selectively dissolved in aqua regia, leaving positively-charged single atoms and clusters on the support because of their stronger metal-support interaction. Indeed, Pt NPs could be selectively removed after optimization of the concentration of aqua regia. After treatment of the catalyst with 1 M aqua regia, DRIFTS results showed that the peak at 2057 cm⁻¹ disappeared, corresponding to the removal of Pt NPs (Fig. S14). The new peak at 2075 cm⁻¹ could be attributed to a

Table 1. Hydrogenation of common functional groups over Pt catalysts.										
Entry	Substrate	Catalyst	Major products (% selectivity)	S.A. ^a (mol _{sub} /mol _{Pt} h)	TOF (h⁻¹)					
1 ^{<i>b</i>}	PhAc	A	Styrene, 94 Ethylbenzene, 6	3888	16336					
2 ^{<i>b</i>}	PhAc	A-C	Styrene, 85 Ethylbenzene, 15	315	15517					
3 ^b	Nitrobenzene	A	Nitrosobenzene, 25 Aniline, 47 Azoxybenzene, 28	7552	31731					
4 ^{<i>b</i>}	Nitrobenzene	A-C	Aniline, 100	208	10246					
5 ^c	Benzaldehyde	А	Benzyl alcohol, 100	391	1643					
6 ^c	Benzaldehyde	A-C	Benzyl alcohol, 100	23	1133					

^a S.A. stands for specific activity. Reaction conditions: 2 mL methanol, 10 bar H₂. ^b substrate/Pt = 4000, room temperature, 15 min. ^c substrate/Pt = 500, 50 °C, 1 h. A: 0.2Pt-SBA-15-500, A-C: 0.2Pt-SBA-15-500-C.

Group	Substrate	Product	Catalyst	<i>T</i> (°C)/H ₂ (bar)	Substrate/Pt	TOF (h ⁻¹)	Ref
-C≡C	PhAc	styrene	Pt/KCC-1	RT/10	1950	366	[18]
	PhAc	ethylbenzene	Pt/KCC-1	RT/10	1950	73	[18]
	PhAc	styrene	Pt-PMA/AC	RT/10	1000	492	[15a]
-NO ₂	4-chloronitrobenzene	4-chloroaniline	Pt-CNF-P	RT/10	1220	610	[19]
	3-nitrostyrene	3-vinylaniline	Pt-Q@IL	50/5	500	1300	[20]
	3-nitrostyrene	3-vinylaniline	Pt/FeO _x	40/3	1250	1500	[16a]
	nitrobenzene	aniline	Pt-NHCs	30/1	2000	4900	[21]
	nitrobenzene	aniline	Pt/KCC-1	RT/10	1950	325	[18]
	nitrobenzene	aniline	Pt-PMA/AC	RT/10	2000	774	[15a]
-CHO	benzaldehyde	benzyl alcohol	Pt/MgAl ₂ O ₄	40/1	590	56	[22]
	4-hydroxybenzaldehyde	4-hydroxybenzyl alcohol	Pt/MgAl ₂ O ₄	40/1	590	22	[22]

FULL PAPER

mixture of single Pt atoms and clusters in oxidized state. After hydrogen reduction of the sample at 200 °C, the peak shifted toward a higher value at 2085 cm⁻¹ with a shoulder at 2076 cm⁻¹, suggesting the presence of single Pt atoms and clusters in reduced state. After the selective leaching of Pt NPs, the catalyst showed a small decrease in specific activities, but the selectivity for the semihydrogenation product was increased (Table S7 and S8), characteristic of single atom catalysts based on earlier studies.^[13, 24] The decrease in activity of the acid-leached samples could be attributed to the higher oxidation state of Pt species (Fig. S14(b vs. d)). However, the activity could be recovered after treating the sample with hydrogen as the Pt species returned to their initial oxidation state. This highlighted that our method is applicable to single atom and sub-nanocluster catalyst on an inert support with higher metal loading, by providing a simple postleaching treatment. In order to gain further understanding on the mechanism of the here investigated hydrogenation reactions, we plan to conduct parahydrogen-induced polarisation experiments. They have been previously proven to provide insight into the pairwise hydrogen addition route on atomically dispersed^[25] and nanoparticle^[26] catalysts. Different reaction pathways between the platinum single-atom and subnanometric catalysts are possible.

Conclusions

In summary, we have presented an effective method to synthesize single atom and sub-nanometric Pt catalysts over an inert silica support. High thermal stability of designed Pt(TBTP) complex, and its ability to partially retain carbon and nitrogen after decomposition, were key to achieving well-dispersed, uniform Pt species on SBA-15. The advantage of the synthetic protocol was clearly proven by comparing the dispersion and catalytic activities of the new catalyst with the ones derived from conventional simple salt precursor. The catalysts showed exceptional activities and high selectivities in the hydrogenation of different functional groups, indicating that the present method may potentially be extended to the synthesis of a series of highly active catalysts for a wide range of applications in catalysis. Future research endeavours may also be directed to reveal the correlations between surface property and the single-atom/sub-nano-cluster catalytic activity. For instance, the effect of the hydrophobicity/hydrophilicity of the support, which plays a critical role in nanoparticle catalysts^[27], remain to be explored in the current system.

Experimental Section

Preparation of mesoporous SBA-15 silica

Silica SBA-15 was prepared according to the method reported in the previous literature.^[28] Pluronic P123 (6 g) was dissolved in 45 g of water and 180 g of 2 M HCl solution with stirring at room temperature for 30 min. TEOS (12.75 g) was added to the solution with stirring at 308 K for 20 h. The mixture was aged at 363 K for 24 h. The white powder was recovered through filtration, washed

with water and ethanol thoroughly, and dried in air for overnight. The product was then calcined at 873 K for 6 h to obtain SBA-15 with the BET surface area of $582 \text{ m}^2 \text{ g}^{-1}$.

Preparation of [Pt(^tBu₃tpy)Cl]Cl complex

The total synthesis was carried out in two steps using previously reported literature.^[29] To prepare the Pt(COD)Cl₂ complex, potassium tetrachloroplatinate (K₂PtCl₄, 2.00 g, 4.8 mmol) was dissolved in a solution of 53.0 mL of water and 63.0 mL of acetic acid. To the light red solution was added 1.6 mL (1.36 g, 12.6 mmol) of 1,5-cyclooctadiene. The reaction mixture was stirred rapidly and heated to 110 °C. Over 3 h the solution became pale yellow and a white precipitate was formed. The volume of the solution was reduced to about 20 mL by evaporation under reduced pressure. The precipitate was collected and washed in succession with small portions of water, ethanol, and diethyl ether. The product was dried in vacuum to give white needles (1.71 g, 95% yield).



In the following step, a portion of Pt(COD)Cl₂ (286 mg, 0.76 mmol) and 'Bu₃tpy (317 mg, 0.79 mmol) were stirred in 40 mL H₂O, 15 mL MeOH and 2 mL acetone in air at 80 °C. A yellow solution and undissolved white reactant were evident after 12 h of stirring. After ~48 h of stirring the solution was filtered over Celite to remove a minute amount of undissolved starting materials and the methanol and acetone were removed in vacuum. The product was extracted into CH₂Cl₂ to produce a yellow organic layer and a cloudy white aqueous layer. The CH₂Cl₂ was removed in vacuum to produce a yellow powder. The powder was washed with diethyl ether to give a yield of 93%. The product [Pt('Bu₃tpy)Cl]Cl was characterized using ¹H NMR and ESI-MS, and in agreement with literature.^[29] Purity check was carried using elemental analyses and in good agreement with the predicted values (Table S3).



Preparation of Pt-SBA-15 catalysts from Pt-TBTP precursor

Required amount of Pt-TBTP complex was dissolved in 5 mL methanol and pretreated SBA-15 (0.45 g) was added in this solution. The mixture was sonicated for 10 min and then vigorously stirred at room temperature for another 30 min. 30 μ L of 0.5 M NaOH solution was added in the solution and stirring was continued for 1 h. The mixture was washed with methanol and centrifuged at 7000 rpm to collect the solid product, which was dried at 50 °C for overnight. The powder sample was then treated at 500 °C for 2 h at a heating rate of 10 °C/min under N₂

atmosphere. The catalyst with x wt% Pt loading was designated as xPt-SBA-15-500.

Preparation of controlled Pt-SBA-15 catalysts from H_2PtCl_6 precursor

Required amount of H_2PtCl_6 was dissolved in 5 mL methanol and pretreated SBA-15 (0.45 g) was added in this solution. The mixture was sonicated for 10 min and then vigorously stirred at room temperature for another 30 min. Minimum amount μ L of 0.5 M NaOH solution was added in the solution at stirring condition to fully adsorb the platinum salt on SBA-15. The mixture was washed with methanol and centrifuged at 7000 rpm to collect the solid product, which was dried at 50 °C for overnight. The powder sample was then treated at 500 °C for 2 h at a heating rate of 10 °C/min under N₂ atmosphere. The catalyst with x wt% Pt loading was designated as xPt-SBA-15-500-C (C denotes controlled sample).

Selective leaching of Pt NPs.

100 mg of catalyst was added to 2 mL 2 M aqua regia and stirred for 12 h at room temperature. The mixture was centrifuged to separate the catalyst and the solution was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the leached Pt amount. The catalyst was washed several times with distilled water and finally with methanol and oven dried at 50 °C for overnight.

Temperature programmed decomposition

Temperature programmed decomposition of catalyst precursor was measured on a Micromeritics AutoChemII 2920 instrument. Typically, 30 mg of sample was pretreated at 50 °C in pure Helium (15 mL/min) gas flow for 1 h. Subsequently, the temperature was raised from 50 to 900 °C at a rate of 10 °C/min under Helium flow. The effluent gases were analyzed by a mass spectrometer.

Hydrogen-Oxygen titration

H₂-O₂ titration was conducted on a ChemBET Pulsar TPR/TPD (Quantachrome). Certain amount of catalyst was pretreated with air at 100 °C for 30 min to remove the hydrogen atoms adsorbed (if any) on Pt atoms. After that, N₂ was used as carrier gas at 80 mL min⁻¹, and the successive doses of H₂ gas were subsequently introduced into N₂ stream by means of a calibrated injection valve (159 μ L H₂ pulse⁻¹) at 100 °C. The titration will end when the intensities of three peaks in a row keep constant. In principle, the titration should follow this equation: PtO (surface) + 3/2 H₂ = PtH (surface) + H₂O. Thus the dispersion of Pt (d_{Pt}) should be calculated using this formula: d_{Pt} = 2/3 n (H₂)/n_{total}(Pt).

Diffuse reflectance infrared Fourier transform spectroscopy

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a Thermo Scientific Nicolet iS50 FT-IR spectrometer with a MCT detector, and a

Praying MantisTM high temperature reaction chamber with ZnSe windows. The CO adsorption on Pt-SBA-1-5 samples was performed at room temperature. 5% CO/Ar (UHP) was introduced into the DRIFTS cell at a flow rate of 40 mL min⁻¹. After the CO saturation, N₂ purge at a flow rate of 40 mL min⁻¹ was performed to remove gas phase CO from the DRIFTS cell and then the adsorbed CO on Pt. All the spectra were recorded using 32 scans and a resolution of 4 cm⁻¹.

Transmission electron microscopy

Transmission electron microscopy (TEM) was performed on a JEM 2100F (JEOL, Japan) microscope operated at 200 kV. X-ray diffraction (XRD) analysis was carried out using a Bruker D8 Advance XRay Diffractometer, at a scan rate of 3º min⁻¹. It was operated at 40 kV applying a potential current of 30 mA. X-ray photoelectron spectra (XPS) were recorded on a VG Escalab MKII spectrometer, using a mono Al K α X-ray source (hv = 1486.71 eV, 5 mA, 15 kV), and the calibration was done by setting the C1s peak at 284.5 eV. Electrospray ionization (ESI) mass spectrometric analysis was performed on a Bruker microTOF-Q system. Thermogravimetric analysis was conducted on a DTG-60A thermogravimetry analyser (Shimadzu) under a nitrogen atmosphere. Pt content in the catalysts was determined using an iCAP 6000 series inductively coupled plasma optical emission spectrometer (ICP-OES). Gas chromatography (GC) analysis was done using an Agilent 7890C GC equipped with a HP-5 column and a flame ionization detector (FID) detector.

X-ray absorption spectroscopy

Pt L₃-edge X-ray absorption spectra (XAS) of supported catalysts and references (Pt foil and PtO₂) were recorded at the BL01B1 beamline at the Spring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan) in the transmission mode at ambient temperature. Data analysis was carried out with Athena and Artemis included in the Ifeffit and Demeter package. For curvefitting analysis on extended X-ray absorption fine structure (EXAFS) spectra, each theoretical scattering path was generated with FEFF 6.0 L. The k^3 -weighted EXAFS oscillation in the range of 3.0–13 Å⁻¹ was Fourier transformed.

Hydrogenation of phenylacetylene

Required amount of phenylacetylene, catalyst and solvent were charged into a 20 mL autoclave reactor. The reactor was then flushed with purified H_2 for three times and finally filled with 10 bar of H_2 . The reaction was performed at room temperature with a stirring speed of 1000 rpm. After completion of the reaction, H_2 pressure was released and products were analysed by GC.

Hydrogenation of benzaldehyde

Required amount of benzaldehyde, catalyst and solvent were charged into a 20 mL autoclave reactor. The reactor was then flushed with purified H_2 for three times and finally filled with 10 bar of H_2 . The reaction was performed at desired temperature in a pre-heated oil-bath with a stirring speed of 1000 rpm. After completion of reaction, the reactor was cooled down to room

temperature and H_2 pressure was released, and products were analysed by GC.

Hydrogenation of nitrobenzene

Required amount of nitrobenzene, catalyst and solvent were charged into a 20 mL autoclave reactor. The reactor was then flushed with purified H_2 for three times and finally filled with 10 bar of H_2 . The reaction was performed at room temperature with a stirring speed of 800 rpm. After completion of the reaction, H_2 pressure was released and products were analysed by GC.

Catalytic recycling experiment for the hydrogenation of benzaldehyde

54 mg of catalyst, 14.1 μ L of benzaldehyde and 2 mL of methanol were charged into a 20 mL autoclave reactor. The reactor was then flushed with purified H₂ for three times and finally filled with 10 bar of H₂. The reaction was performed at 50 °C for 1 h in a preheated oil-bath with a stirring speed of 1000 rpm. After completion of reaction, the reactor was cooled down to room temperature and H₂ pressure was released, and products were analysed by GC. The spent catalyst was thoroughly washed with methanol and then used for the next catalytic run.

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Stabilizing the instable: A designed platinum precursor facilitates the synthesis of stable platinum catalysts on an inert support such as silica. A simple post-synthetic step selectively removes platinum nanoparticles and increases the selectivity toward several hydrogenation reactions.

Sudipta De, Maria V. Babak, Max J. Hülsey, Wee Han Ang,* Ning Yan*

Page No. – Page No.

Designed precursor for the controlled synthesis of highly active atomic and sub-nanometric platinum catalysts on mesoporous silica