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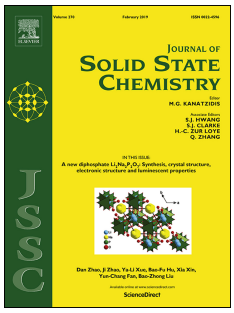

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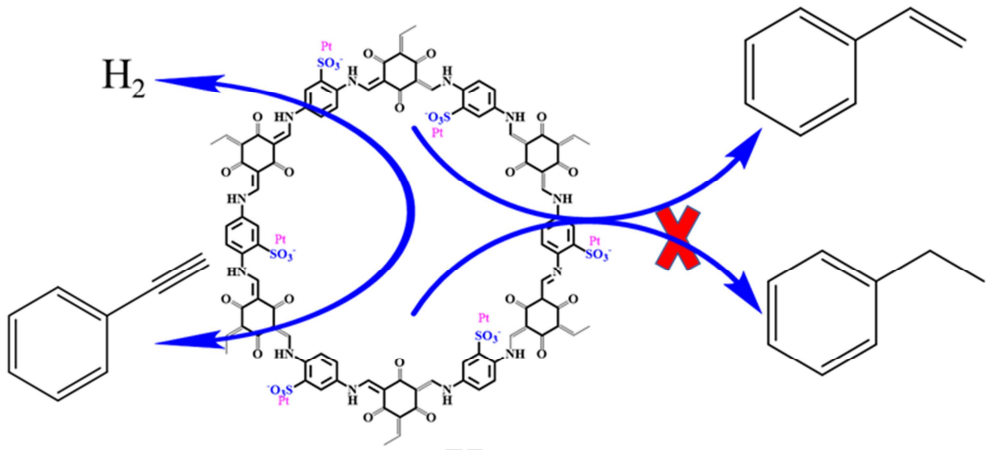
Constructing Pt^{I}@COF for Semi-Hydrogenation Reactions of Phenylacetylene

Jian Hong Li[ab],[†] Zhi Wu Yu[c],[†] Jian Qiang Li[a], Ya Ling Fan[a], Zhi Gao[a], Jian Bo Xiong[a], Li Wang[a], Yuan Tao[a], Li Xiao Yang[a], Yu Xin Xiao[a] and Feng Luo[a*]



A noble catalyst Pt@COF was first prepared, which exhibits remarkable performance for semi-hydrogenation of phenylacetylene, including high selectivity, turnover frequency value, good recycle, strong stability.

Constructing Pt^{I}@COF for Semi-Hydrogenation Reactions of Phenylacetylene

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Abstract: The great efforts have been devoted to fabricate excellent hydrogenation catalysts owing to the broad applications in industrial fields. However, the preparation processes of traditional hydrogenation catalysts are often complicated. Herein, mono-valence Pt^{I}@COF was synthesized as a catalyst for semi-hydrogenation of phenylacetylene for the first time. The easily prepared SO_3H-linked COF possesses a two-dimensional eclipsed layered-sheet structure, making its incorporation with metal ions feasible. The as-prepared Pt^{I}@COF composite exhibits excellent performance for semi-hydrogenation phenylacetylene with 93.5% conversion and 90.2% selectivity to styrene under mild reaction conditions (1 bar H_2, 25℃) within 20 min. It's worth noting that the turnover frequency (TOF) value reaches at 3965 h^{-1}, which outperforms most of recently reported excellent Pt-based catalysts for this reaction.

Keywords: hydrogenation catalysts; Pt^{I}@COF; turnover frequency; mono-valence.

1. Introduction

As a harmful material in polymerization of styrene, phenylacetylene readily results in catalyst poisoning during styrene polymerization and thus affects properties of polystyrene. In this sense, removing phenylacetylene *via* selective hydrogenation process is necessary for improving qualities of polymerized styrene materials .**[1-3]** However, the selectivity to the desired styrene is usually unsatisfied because of the easy generation of over-hydrogenation product phenylethane.**[4-5]**Up to now, intensive research endeavors have been devoted to develop excellent catalysts for selective hydrogenation of phenylacetylene to styrene. It was found that noble metal (Pt, Pd, Au etc.) catalysts are the ideal choice because of their high catalytic activity and durable stability.`**[6-10]** Amongst Pd-based materials are used intensively in the hydrogenation of phenylacetylene because of their strong dissociative ability for H_2.**[11]** However, some shortcomes, such as unsatisfied catalytic selectivity, high metal content and long reaction time, hinder their industrial applications.**[12-25]** Thus, developing new catalysts for efficiently catalyzed hydrogenation of phenylacetylene is urgent.

To date, Pt-based catalysts loaded on different supports including carbon nanotubes, **[26-27]** triphenylphosphine polymer,**[28]** resin,**[29]** zeolite-templated carbon**[20]** were investigated for semi-hydrogenation of phenylacetylene. For example, Li *et al*. reported a CNT-supported Pt catalyst (Pt/CNTs) for hydrogenation of phenylacetylene, where the conversion and the selectivity of styrene can reach at 98% and 86%, respectively.[17] Pt/$PSiO_2$ catalyst reported by Fukuoka *et al.* exhibited 99.1% conversion of phenylacetylene and 99.5% selectivity to styrene.**[30]** Nevertheless, the low intrinsic activity (TOF value) of these catalysts stimulate us to design new catalysts. For

aforementioned Pt-based catalysts, their catalytic activities were realized by reduction of the Pt^{2+} species to zero valence Pt (Pt^0), which endowed the metal active site for catalysis. In contrast to the zero-valence state Pt^0, mono-valence Pt^I metal composite, which may improve the instrical activity of Pt-based catalysts, has not been studied for catalyzing hydrogenation of phenylacetylene ever.

In recent years, covalent organic frameworks (COFs) have attracted considerable interest since the first discovery by Yaghi and co-workers in 2005,**[31]** which comprised of periodically extended and covalently bound crystalline porous network structures.**[32]** Our group has synthesized a novel material named COF-SO_3H for uranium extraction from sea water, in which the COF-SO_3H can bear strong acid and alkali.**[33-34]** Thus, we believe that COF-SO_3H should be excellent support to prepare Pt-based catalysts, which are not well investigated in heterogeneous catalysis.

Herein, an ammonium-modified material of $[NH_4]^+$ $[COF\text{-}SO_3^-]$ as a support to load Pt nanoparticles for semi-hydrogenation of phenylacetylene was studied. Apart from stabilizing Pt nanoparticles, the $[NH_4]^+[COF\text{-}SO_3^-]$ can also form strong chelates with Pt^+ and thus enhances the activity.**[35]**

2. Experimental section

2.1 Synthesis of catalysts

2.1.1 Synthesis of 1,3,5-triformylphloroglucinol

The ligand material 1,3,5-triformylphloroglucinol was synthesized in the light of the reported literature.**[36]** Firstly, the hexamethylenetetramine (15.098g, 108mmol) and dried phloroglucinol (6.014g, 49mmol) were added in a three-necked round-bottomed flask with 90mL trifluoroacetic acid. Then the mixture solution was stirred for 2h at 100ºC under N_2 condition in oil bath pan. 150mL 3mol/L HCl was added in the flask and continued to stir 2h. After that, the mixture solution

was filtered by kieselguhr and extracted with dichloromethane at room temperature. The obtained yellow solution was steamed using rotary evaporation at 50ºC and washed with hot ethanol after dried over magnesium sulfate. Finally, the yellow powder was obtained after dried under vacuum.

2.1.2 Synthesis of 2, 5-dihydroxy benzenesulfonate amine

Briefly, 63mg 1,3,5-triformylphloroglucinol and 84.7mg 2, 5-diaminobenzene sulfonic acid, 3mL N-butyl alcohol and 3mL o-dichlorobenzene were added to a 100 mL Schlenk tube in order. After that the turbid solution was flash frozen in liquid nitrogen for three times after added acetic acid(0.5mL,3mol/L). In the end, the tube was put into the muffle and set the temperature slowly raised to 120 at 10□/min. The reaction was kept 120°C for 3 days and cooled to room temperature at 6°C/h. Crimson powders were obtained by centrifugation with acetone and dried under vacuum.

2.1.3 Synthesis of $[NH_4]^+[COF\text{-}SO_3^-]$

The ion-exchange material of $[NH_4]^+[COF\text{-}SO_3^-]$ is obtained by immerging $COF\text{-}SO_3H$ in $NH_3 \cdot H_2O$(1%) for 24 h and washed by water and methanol. Crimson powders were obtained by centrifugation with acetone and dried under vacuum.

2.1.4 Synthesis of Pt^I@COF

The catalyst material was synthesized as followed. 100mg $[NH_4]^+[COF\text{-}SO_3^-]$ is dispersed in 14mL deionized water and then added 400uL 0.125mol/L $[Pt(NH_3)_4](NO_3)_2$ stirring for 2h. After that, the mixture washed by deionized water and methanol and dried at drying oven. Then, the dried power is dispersed in 14mL deionized water and dropwise $NaBH_4$(4mL 1mol/L) to reduce for 6 h under N_2 atmosphere. Finally, the crimson power sample was washed and dried at 60°C overnight and marked as $[NH_4]^+[COF\text{-}SO_3^-]$. The content of Pt in $[NH_4]^+[COF\text{-}SO_3^-]$ is around 0.83 wt.% confirmed by ICP.

2.1.5 Synthesis of Pt^0@COF

The prepared Pt^0@COF was obtained by $NaBH_4$(4mL 1mol/L) sprayed into $[Pt(NH_3)_4](NO_3)_2$(400uL 0.125mol/L) solution for stirring at N_2 atmosphere. After that, the 100mg $[NH_4]^+[COF\text{-}SO_3^-]$was added and stirring for 2h. Finally, the mixture solution was dried under vacuum oven at 60℃.

2.2 Characterization

The morphologies of the material were obtained by SEM-EDS (scanning electron microscope-Energy Dispersive Spectrometer) measurements using a Hitachi S-4800 microscope. The powder data were collected by PXRD (X-ray powder diffraction) using a Bruker AXS D8 Discover powder diffractometer with monochromatized Cu-Kαradiation (at 40 kV, 40 mA, λ = 1.5406Å) in the rang of 2θ = 3–85° with a step size of 0.018 and a count time of 5 s per step. The simulated powder patterns were calculated by Mercury 1.4. IR (Infrared Spectra) measurements were measured by a Bruker VERTEX 70 spectrometer in the 500-4000 cm^{-1} region. X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB250 spectrometer. The gas adsorption isotherms were collected on a Belsorp-max. Ultrahigh-purity-grade (>99.999%) N_2 gases were used during the adsorption measurement. The Pt content in catalyst was measured by inductively coupled plasma-mass spectroscopy (ICP-MS, NexION 300X). The catalytic reaction was traced and identified by gas chromatography (GC, Agilent 7890A with a 0.25 mm×30 m DB-5 capillary column) using an internal standard technique. Transmission electron microscopy (TEM) micrographs were collected on a FEI Tecnai G2 F20 transmission electron microscope at an accelerating voltage of 200 kV.

2.3 Catalyst test

2.3.1 General Procedure for the Catalytic Hydrogenation of Phenylacetylene

In a typical procedure for catalytic activity test of Pt^{I}@COF, 114uL (1mmol) of phenylacetylene, 15 mg of catalyst and 15 mL of ethanol as solvent were charged into a three-necked, round-bottomed flask. Afterwards, the flask was purged with 1 MPa H_2 for several minutes to allow pure H_2 atmosphere for the reaction. At this time, the mixture was magnetically stirred at 25 ºC temperature and the reaction time was calculated at this point. Samples with 0.5 mL withdrawn at regular intervals of reaction time were analyzed by GC (GC-2014) equipped with an FID detector and a capillary column (DB-5, 30 m 0.45 mm 0.42 mm). The conversion, selectivity and turnover frequency (TOF) were calculated on basis of the following equations:

$$\text{Conversion }\% = \frac{\text{Phenylacetylene feed(mol)} - \text{Phenylacetylene residue(mol)}}{\text{Phenylacetylene feed(mol)}} \times 100\%$$

$$\text{Selectivity }\% = \frac{\text{Styrene product(m0l)}}{\text{Phenylacetylene feed(mol)} - \text{Phenylacetylene residue(mol)}} \times 100\%$$

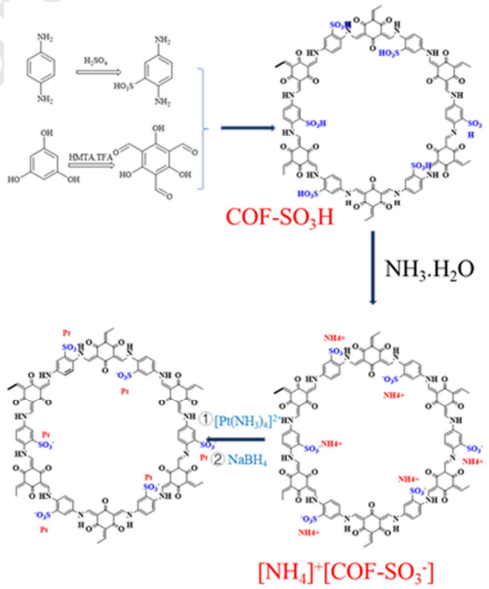
$$\text{TOF}(h^{-1}) = (n_{\text{Phenylacetylene}} \times C_{\text{conversion}} \times C_{\text{selectivity}}) / n_{Pt} \times t$$

2.3.2 Reuse experiment

In the reuse experiment, the catalyst was isolated by centrifugation and washed with ethanol and dried at 70°C under vacuum. The same amount of phenylacetylene was added at every catalytic reaction. After every catalytic reaction, the conversion and the selectivity of the products were determined by GC.

3. Results and discussion

As depicted in **scheme 1**, the synthesis of Pt^{I}@COF includes four steps. Firstly, COF-SO_3H was prepared through condensation between 1,3,5-triformylphloroglucinol and 2,5-diaminobenzene sulfonic acid by the solvothermal method. Then the COF-SO_3H was aminated by $NH_3 \cdot H_2O$ to obtain $[NH_4]^+[COF\text{-}SO_3^-]$. After that, the metal precursor $[Pt(NH_3)_4](NO_3)_2$ solution of Pt^{2+} was deposited in the $[NH_4]^+[COF\text{-}SO_3^-]$ material by ion exchange. Finally, Pt^{2+} was reduced to Pt^{I} under N_2 atmosphere using $NaBH_4$ as reducing agent. A series of characterizations were carried out for COF-SO_3H、 $[NH_4]^+[COF\text{-}SO_3^-]$ and Pt^{I}@COF. The powder X-ray diffraction (PXRD) data of COF-SO_3H and $[NH_4]^+[COF\text{-}SO_3^-]$ agree with the simulated one by Material Studio Forcite molecular dynamics method **(Fig. 1a)**. ^{13}C CP-MAS solid-state NMR spectroscopy **(Fig. 2)** further proves the β-ketoenamine-linked structure in COF-SO_3H.**[32]** $[NH_4]^+[COF\text{-}SO_3^-]$ immersed in strong acid, boiling water and strong base was characterized by PXRD testes. The results demonstrate that the $[NH_4]^+[COF\text{-}SO_3^-]$ possess high chemical stability.**(Fig. 3b)**



Scheme 1. Synthetic scheme of SO_3H-decorated COF (COF-SO_3H), the ammoniated material of $[NH_4]^+[COF\text{-}SO_3^-]$ and Pt-loaded material of Pt^{I}@COF.

From the PXRD patterns **(Fig. 1b)** of Pt^{I}@COF, three intense peaks were found at 40°, 46° and 67°, which were arranged to the (111), (200) and (220) reflections of face-centered cubic (fcc) Pt crystal (JCPDS card, No. 04-0802), indicating the formation of Pt nanoparticles.**[32]** SEM image revealed that Pt^{I}@COF still can keep the uniform fiber morphology as observed for COF-SO_3H and $[NH_4]^+[COF\text{-}SO_3^-]$. **(Fig. 4)** The character peak of -C-N (~1213 m^{-1}) and -C=C (~1567 cm^{-1}) was discovered from the FTIR spectrum of Pt^{I}@COF, which almost identical to that of $[NH_4]^+[COF\text{-}SO_3^-]$. Noteworthy, disappearance of NH_4^+ with hydrogen bonds at 3210 cm^{-1}comfirmed the ion exchange between Pt and $[NH_4]^+$. **(Fig. 5)**

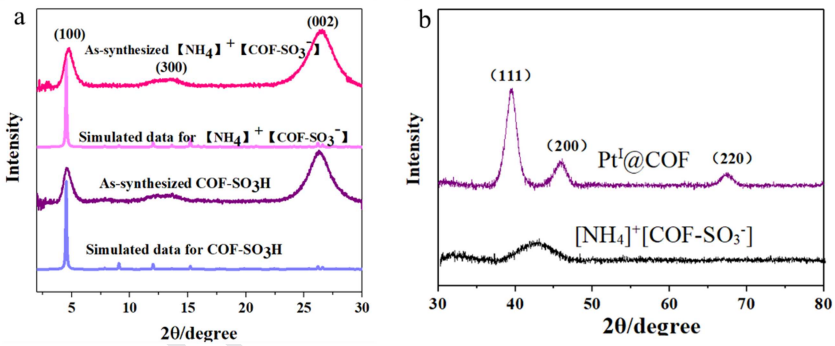


Fig. 1 a) The experimental and calculated PXRD patterns of COF-SO_3H and $[NH_4]^+[COF\text{-}SO_3^-]$. b) XRD patterns of $[NH_4]^+[COF\text{-}SO_3^-]$ and Pt^{I}@COF.

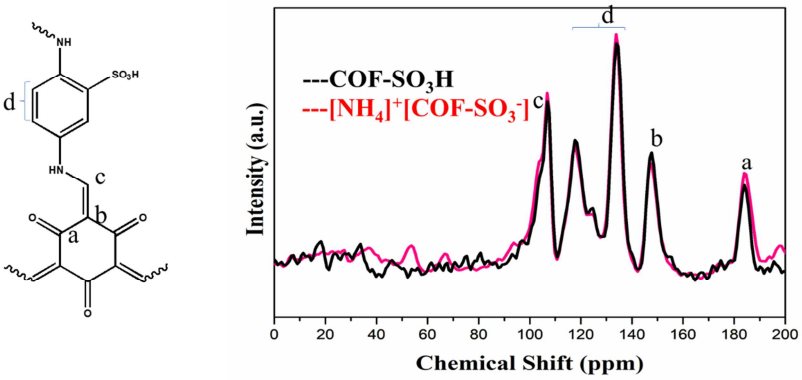


Fig. 2 ^{13}C CP-MAS spectrum of COF-SO_3H and $[NH_4]^+[COF\text{-}SO_3^-]$.

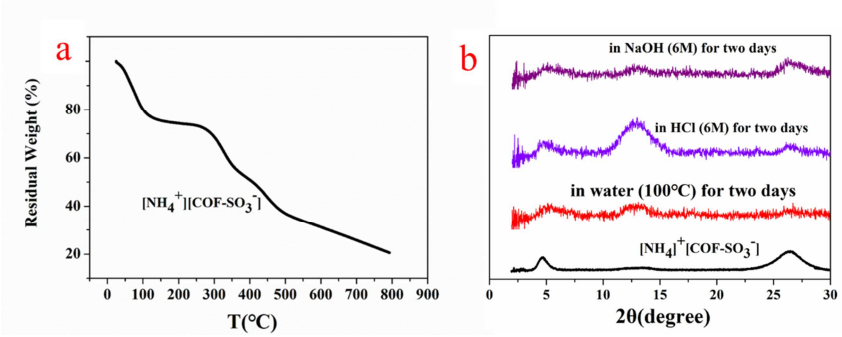


Fig. 3 a) TGA of $[NH_4^+][COF\text{-}SO_3^-]$, b) The chemostability of $[NH_4]^+[COF\text{-}SO_3^-]$ under boiling water, strong acid and strong base by PXRD patterns.

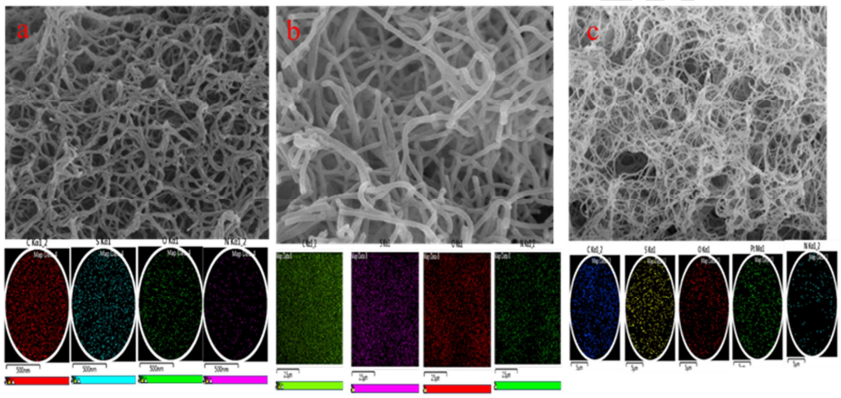


Fig. 4 The SEM images and EDS mapping results of a)$COF\text{-}SO_3H$, b) $[NH_4]^+[COF\text{-}SO_3^-]$ and c) Pt^I@COF, respectively.

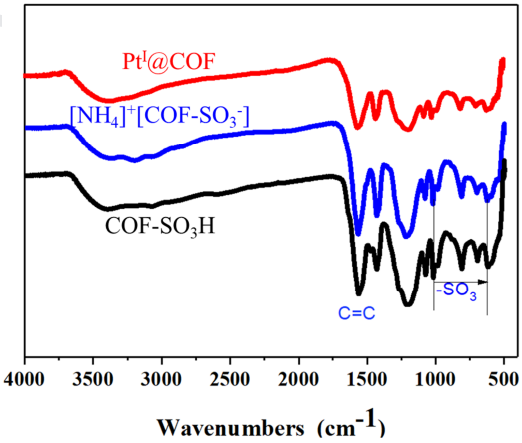


Fig. 5 FT-IR spectra of $COF\text{-}SO_3H$、$[NH_4]^+[COF\text{-}SO_3^-]$ and Pt^I@COF.

X-ray photoelectron spectroscopy (XPS) analysis of Pt^I@COF was used to probe the chemical valence state of Pt. Quantitative X-ray photoelectron spectroscopy (XPS) **(Fig. 6)** shows that most

of the Pt^{2+} atoms have been reduced to Pt^{+} after treatmenting with $NaBH_4$, and this value fits better with that of unsaturated Pt^{+} species confined in MOFs**[37]** or ligated to thiols,**[38]** which corresponds to formal Pt^{+} rather than to any typical signal for Pt(0).**[39]**

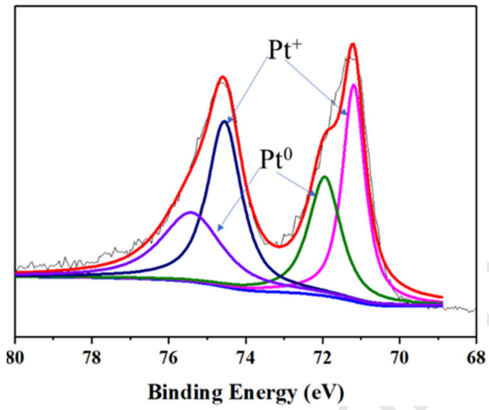


Fig. 6 XPS spectra of Pt 4f electrons of Pt^{I}@COF.

Compared with $[NH_4]^{+}[COF\text{-}SO_3^{-}]$, the N_2 adsorption capacity at 77 K is largely reduced after Pt-loaded in sample, giving a BET surface area of 51 m^2/g, most likely due to the occupation of pore by Pt nanoparticles **(Fig. 7)**. TEM technique was used to characterize the particle sizes of Pt on $[NH_4]^{+}[COF\text{-}SO_3^{-}]$ **(Fig. 8)**. As shown in Fig. 8, Pt^{I}@COF are still keep the filiform morphology and Pt NPs uniformly distributed on the surface of material. The average size of Pt NPs in Pt^{I}@COF is about 4.6 nm as displayed in Fig.8. The formation of metal NPs, especially for noble metals, is difficult but important to improve the usage efficiency of expensive metal NPs. The formation of small Pt clusters on Pt^{I}@COF is possibly due to the coordination ability of the sulfonate ligand to Pt NPs. The thermogravimetric analysis (TGA) demonstrates that Pt^{I}@COF owns excellent thermal stabilities up to 300 □ **(Fig. 9)**, which provides the demands for potential applications in catalysis. Inductively coupled plasma (ICP) analysis demonstrates that the Pt content in the sample is 0.83 wt.%, which is close to that determined by SEM-EDS spectrum **(Table 1)**.

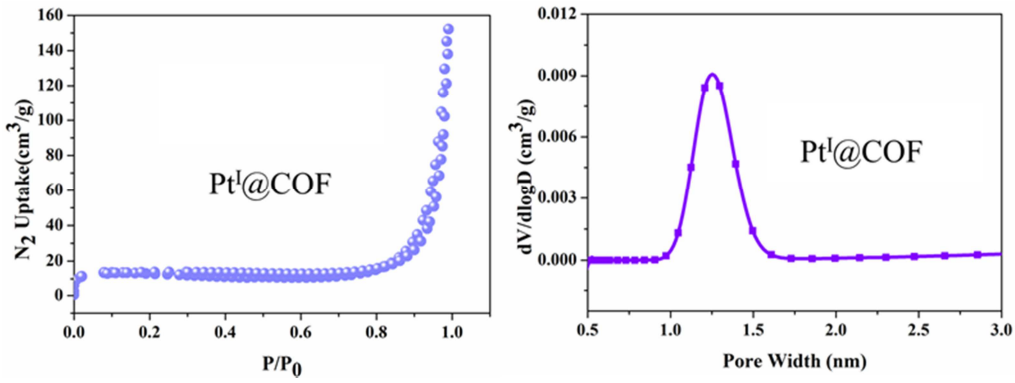


Fig. 7 The N_2 adsorption–desorption at 77K for Pt^I@COF with the insert of distribution of pore size.

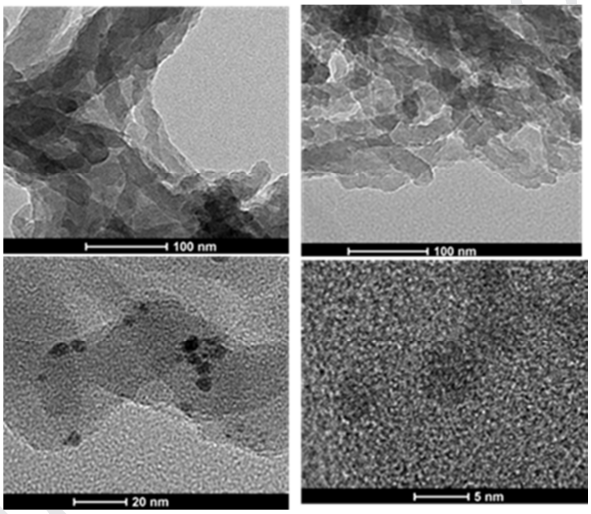


Fig. 8 STEM images of Pt^I@COF.

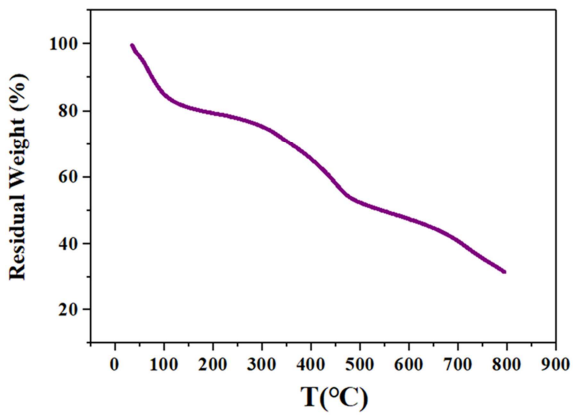


Fig. 9 TGA of Pt^I@COF.

Table 1. The element contents of the as- Pt^I@COF.

Element	C	N	O	S	Pt	Total
Content(wt.%)[a]	58.86	23.36	12.08	4.87	0.83	100.00
Content(wt.%)[b]	56.75	25.13	11.79	5.42	0.91	100.00

[a] determined by element analysis

[b] determined by SEM-EDS spectrum

To test the catalytic activity of Pt^{I}@COF, selective hydrogenation of phenylacetylene was performed. which was carried out with 114 uL of phenylacetylene, 15.0 mg of the catalyst, and 15 mL of ethanol in a 50mL three-necked round-bottomed flask under controlled H_2 pressures and temperatures. **Fig. 10** shows the conversion of phenylacetylene and selectivity for styrene by the Pt catalysts under the conditions of 1 bar H_2 at different temperature. The Pt^{I}@COF catalyst afforded 93.5% phenylacetylene conversion and 90.2% styrene selectivity in 20 min, which was apparently the best among the tested temperatures at 25 □. The kinetic curve of Pt^{I}@COF indicates that the reaction rate is fast in the initial 20 min without any induction time. Within 40 min, 100% conversion was achieved.

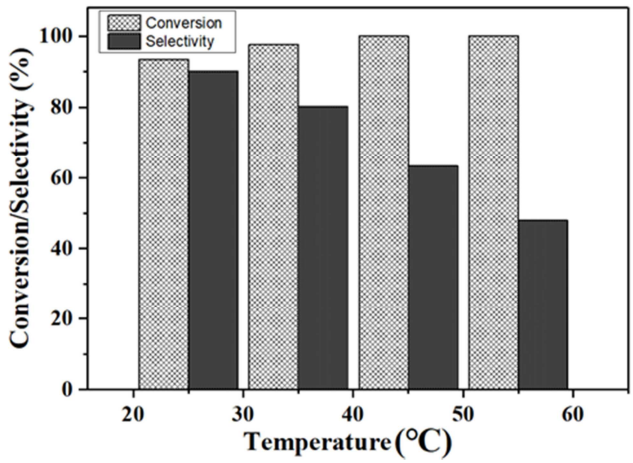


Fig. 10 The conversion of phenylacetylene and selectivity for styrene by Pt^{I}@COF over the different temperature.

To disclose the catalytic mechanism, a comparison experiments are carried out. Under similar reaction conditions, Pt^{2+}@COF (prepared by impregnation of $[Pt(NH_3)_4](NO_3)_2$ on $[NH_4]^+[COF\text{-}SO_3^-]$ without reduction)、Pt^0@COF (prepared by spraying method)**[40-41]** and the pristine $[NH_4]^+[COF\text{-}SO_3^-]$ were applied to semi-hydrogenation of phenylacetylene. Seen from **Table 2**, Pt including in Pt^{2+}, Pt^+ and Pt^0 shows high catalytic activity for hydrogenation reaction of phenylacetylene. However, only the Pt^I@COF catalyst performs high selectivity. Accordingly, Pt^+ loaded on support could be a good candidate for semi-hydrogenation of phenylacetylene. In addition, seen from **Table 3**, by comparing with the reported semi-hydrogenation experiments of alkynes based on Pt catalyst in the literature, it is clearly suggesting that our catalyst presents a highly rare example showing both high selectivity and conversion for semi-hydrogenation. Most importantly, ultrahigh catalytic efficiency for the Pt^I@COF catalyst evaluated by the turnover frequency value is up to 3965 h^{-1}, which outperforms most of reported catalysts for such use.

Table 2. Selective hydrogenation of phenylacetylene to styrene on different catalysts.

Catalysts	t (min)	Conversion (%)	Selectivity to styrene (%)
$[NH_4]^+[COF\text{-}SO_3^-]$	20	2.4	100.0
Pt^{2+}@COF	72	99.8	8.5
Pt^0@COF	20	85.8	47.8
Pt^I@COF	20	93.5	90.2

Table 3. A comparison with other reported catalysts for hydrogenation of alkyne.

Catalyst	H_2(bar)	t(min)	T(℃)	C(%)	S(%)	TOF(h^{-1})	Ref
Pt^I@COF	1	20	25	93.5	90.2	3965	This work
Pt/oCNTs	0.4	60	50	98	86	43	17
Ru@Pt/oCNTs	0.4	60	50	88	88	132	17
Pt/$PSiO_2$	20	120	45	99.1	99.5	2304	20
CN@Pt/CNTs	0.3	120	50	100	90	812	29
Pt@ZTC	0.5	60	50	63	85	4766	30

MPF-SO_3H-Pt	1	15	80	43	89	930	31
Pt	1	550	50	30.8	90.2	1368	32a
Pt/ABSFGF	1	9	51	90	69		32b

The recycling stability of Pt^I@COF was also investigated. As shown in **Fig. 11**, neither conversion nor selectivity exhibited any considerable decrease in comparison with the fresh catalyst. This demonstrates that Pt^I@COF is highly stable and durable. To further confirmation the stability of the sample, the XRD and XPS were detected after 1st cycle and 3rd cycle reaction. From **Fig. 12**, it is demonstrated that the crystalline structure is changed slightly after 1st cycle and 3rd cycle reaction. **Fig. 13** shows that after 1st cycle and 3rd cycle reaction, there is almost no remarkable change of the distribution of Pt NPs in the used Pt^I@COF catalyst. Above results indicate the Pt^I@COF has high stability. Meanwhile, **Fig. 14** shows the change of Pt^0 of Pt^0@COF after used. As shown in **Table 4**, it further demonstrates the Pt@COF presents excellent catalytic performance under mild reaction conditions for various alkynes, suggesting its superior application in this field.

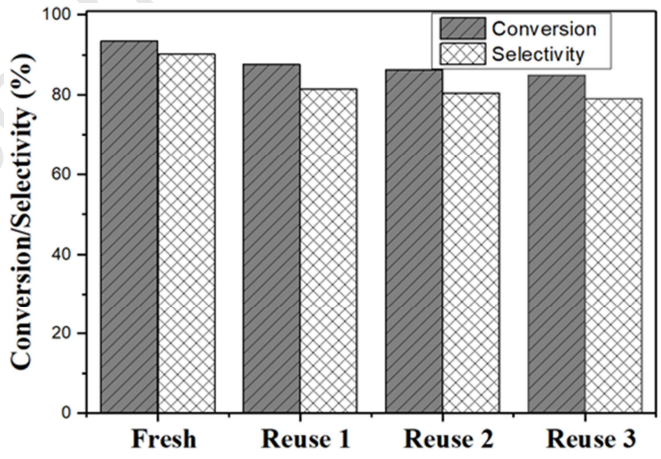


Fig. 11 The recyclability of Pt^I@COF catalyst.

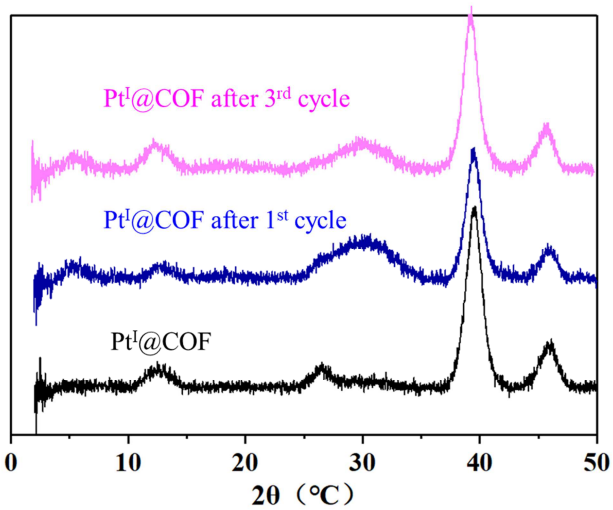


Fig. 12 PXRD patterns of different samples.

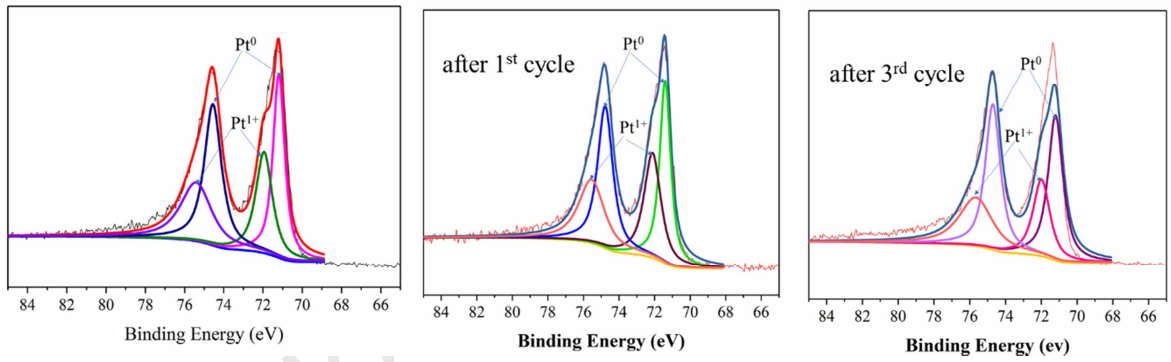


Fig. 13 XPS spectra of different samples for Pt^{I}@COF.

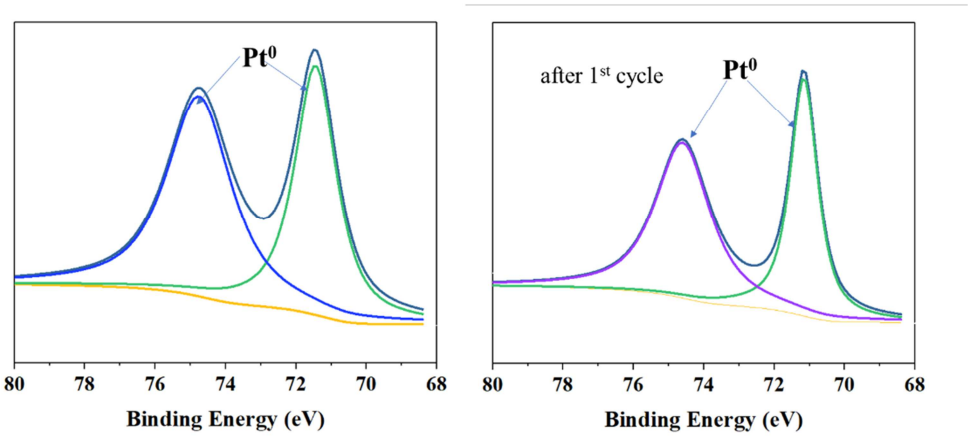
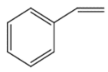
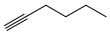
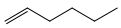
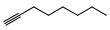
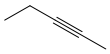


Fig. 14 XPS spectra of different samples for Pt^{0}@COF.

Table 4. Semi-hydrogenation of various alkynes catalyzed by Pt□@COF catalyst.

Entry	Substrate	Time (min)	Product	Conversion (%)	Selectivity (%)
1		20		93.5	90.2
2		120		92.0	89.5
3		80		91.0	90.4
4		25	4-Octene and isomer alkenes	94.0	90.0
5		40	2-pentene and isomer alkenes	92.0	88.7

4. Conclusions

In conclusion, COF-supported catalyst of Pt^{I}@COF was synthesized by a simple impregnation-reduction method as a novel catalyst for selectively catalyzing hydrogenation of phenylacetylene. It is the first time to prepare the mono-valence Pt^{I}@COF. And the outstanding catalytic performance is achieved with 93.5% conversion and 90.2% selectivity to styrene under extremely mild reaction conditions (1 bar H_2, 25□). Noticeably, the turnover frequency (TOF) value is as high as 3965 h^{-1}, which exceeds most of reported Pt-based catalysts. A series of experimental and characterization results disclose that Pt^{+} on COF can provide not only more accessible active sites for phenylacetylene conversion, but also allow for high selectivity. Moreover, the as-fabricated Pt^{I}@COF also shows high stability without obvious loss even after three successive runs. This work provides a novel strategy for the fundamental design of COF-supported metal catalysts and thereby provides a new avenue for the fabrication of catalytic materials.

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Highlights:

1.This work presents the first case of mono-valence Pt^{I}@COF for semi-hydrogenation reactions of phenylacetylene.

2.This work firstly present a simple impregnation-reduction method for the preparation of Pt-anchored covalent organic framework (Pt^{I}@COF).

3. Pt^{+} and Pt^{0} can synergistically promote the transformation of phenylacetylene to styrene.

4. The Pt^{I}@COF exhibits remarkable performance with 93.5% conversion and 90.2% selectivity to styrene under mild reaction conditions (1 bar H_2, 25 ℃).

5.This kind of material is highly repeatable for such use.

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: