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# **Accepted Article** Title: Platinum-supported zirconia nanotube arrays supported on graphene aerogels modified with metal-organic frameworks: adsorption and oxidation of formaldehyde at room temperature Authors: Haocun Tan, Dongyun Chen, Najun Li, Qingfeng Xu, Hua Li, Jinghui He, and Jian-Mei Lu This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201904426 Link to VoR: http://dx.doi.org/10.1002/chem.201904426

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# Platinum-supported zirconia nanotube arrays supported on graphene aerogels modified with metal-organic frameworks: adsorption and oxidation of formaldehyde at room temperature

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Abstract: The precious metal catalyst (such Au, Pd, Rh, Ag, Ru, Pt and Pd) which was supported on transition metal oxide (for example, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, TiO<sub>2</sub> and NiO) can effectively oxidize VOCs. In this study, porous platinum-supported zirconia materials were prepared by a "surface-casting" method. The synthesized catalyst presents an ordered nanotube structure and exhibits excellent performance toward the catalytic oxidation of formaldehyde. Herein, a facile method, utilizing a boiling water bath, was used to fabricate graphene aerogels (GA), and a macroscopic 3D Pt/ZrO<sub>2</sub>-GA was modified by introducing an adjustable MOF coating via a surface step-by-step method. The unblocked mesoporous structure of the graphene aerogel facilitates the ingress and egress of reactants and product molecules. The selected MOF-5 composite demonstrates excellent performance for HCHO adsorption. Additionally, the 7wt.% Pt/ZrO2-GA-MOF-5 catalyst achieved ~90% conversion when subjected to a reaction temperature of 70°C (T<sub>90%</sub>=70°C). The Pt/ZrO<sub>2</sub>-GA-MOF-5 composite induces a catalytic cycle, that is, increasing the reaction rate by simultaneously adsorbing and oxidizing HCHO. This work provides a simple way to increase reactant concentration on the catalyst to increase the reaction rate.

## Introduction

Formaldehyde is generally considered to be a toxic indoor air pollutant and one of the most concerned VOCs.<sup>[1, 2]</sup> Typically, formaldehyde is derived from painting and decoration materials, textiles and from smoking.<sup>[3]</sup> Even at lower concentrations (<0.5ppm), HCHO species in the air will cause severe health problems, such as irritating the respiratory system and skin, causing coughs, headaches, cardiovascular disease, and possibly even has some negative impacts on the central nervous system and genetic material.<sup>[4-7]</sup> As people pay more and more attention to the quality of their living environment and their own health, formaldehyde has attracted more and more attention.

Currently, typical methods of eliminating formaldehyde include chemical and physical adsorption,<sup>[8-12]</sup> photocatalytic

degradation<sup>[13-15]</sup> and plasma treatment<sup>[16]</sup>. Among these methods, the most promising is to completely degrade formaldehyde into H<sub>2</sub>O and CO<sub>2</sub> by thermal catalytic oxidation since a higher removal rate is achieved with a lower concentration of secondary pollution by-products.[17-22] The efficiency of noble metal-supported transition metal oxides to remove formaldehyde at room temperature is considerable.<sup>[19, 20,</sup> <sup>23, 24]</sup> A series of noble metal-supported oxides have been used to catalyze formaldehyde degradation such as Pt/TiO2,[25] Pt/Fe<sub>2</sub>O<sub>3</sub>,<sup>[26]</sup> Pt/MnO<sub>2</sub>,<sup>[27]</sup> Pt/MnO<sub>x</sub>-CeO<sub>2</sub>,<sup>[28]</sup> Pd-Mn/Al<sub>2</sub>O<sub>3</sub>,<sup>[29]</sup> Au/TiO<sub>2</sub>,<sup>[30]</sup> Ag/CeO<sub>2</sub>,<sup>[31]</sup> and Ag/Co<sub>3</sub>O<sub>4</sub>.<sup>[32]</sup> Yazawa et al. studied the loading of platinum on a metal oxides (such as La<sub>2</sub>O<sub>3</sub>, MgO,  $ZrO_2$ ,  $Al_2O_3$ ,  $SiO_2-Al_2O_3$ ,  $SiO_2$ , and  $SO_4^{2-}$ - $ZrO_2$ .) to form a catalyst and catalytic oxidation of propane at low temperatures.<sup>[33]</sup> The results show that the stronger the acidity of the platinum-loaded support has higher catalytic activity. Hence, ZrO<sub>2</sub> is selected as the base material to support Pt. Additionally, considering that the active phase of the catalyst should be highly uniformly dispersed and the catalyst easily recycled, the unblocked mesoporous structure of graphene aerogel (GA) has a large specific surface area, which can disperse nanoparticles well and provide excellent channels for gas molecules to enter and exit. In the process of generating aerogel, the catalyst is easily combined with graphene sheets, we construct the aerogel using graphene sheets and add the catalyst thereto before the aerogel is formed.

Recently, the combination of metal-organic framework (MOF) with other catalysts is a hot topic at this stage of research. Many MOFs have excellent adsorption properties because of their considerable pore volume and specific surface area, and its chemical stability. A great deal of MOF materials exhibit excellent adsorption capacity for gases such as formaldehyde, CH<sub>3</sub>OH, hydrogen and CO<sub>2</sub>. Therefore, it is feasible to modify the surface of the catalyst with MOF to increase the catalytic rate. Herein, MOF-5 is dispersed on a GA to improve the HCHO adsorption properties.<sup>[34]</sup>

Hitherto, numerous investigations have reported the catalytic oxidation of HCHO, however, there have been few reports on the modification of the catalyst surface with MOFs to improve CO conversion. In view of this, we disperse MOF on the surface of GO sheets by self-assembly and form aerogel by a simple boiling water bath method (showed in **Scheme 1**). In this work,  $Pt/ZrO_2$ -GA-MOF-5 can simultaneously adsorb and catalyze the oxidation of HCHO, thereby increasing the HCHO oxidation rate.

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Supporting information for this article is given via a link at the end of the document.



Scheme 1. Schematic representation of the synthesis of  $Pt/ZrO_2$ -GA-MOF-5.

### **Results and Discussion**

#### Preparation and characterization of SBA-15-OH and Pt/ZrO<sub>2</sub>

SBA-15-OH, prepared according to a previously reported method, was used as a silica hard template. Thereafter, porous Pt/ZrO2 materials were prepared by a so-called surface-casting method. The SBA-15-OH channels were immersed in the  $H_2PtCl_6 \cdot 6H_2O$  and  $ZrOCl_2 \cdot 8H_2O$  precursor solution bv impregnation. The SBA-15-OH template was then leached out using a hot sodium hydroxide solution. SEM and TEM were used to characterized the surface morphologic structure and structure of the prepared SBA-15-OH and Pt/ZrO2 materials (Figure S1, Figure 1a and Figure 1b). Figures S1a and S1b show a SEM and TEM micrograph, respectively, of the highly ordered mesoporous silica SBA-15-OH. The key to the successful synthesis of highly ordered mesoporous ZrO<sub>2</sub> is the ordered nanotube arrays and the silanol-rich surface of SBA-15-OH. At the same time, it can be clearly observed that the size of the synthesized nanotube arrays is ~10nm. Further observations show that the Pt/ZrO<sub>2</sub> structure (Figure 1b) is similar to that of SBA-15-OH (Figure S1b), indicating that Pt/ZrO<sub>2</sub> was successfully synthesized by the surface-casting method. Furthermore, it is evident that metallic platinum (black dots) is successfully supported on the zirconia nanotube arrays (Figure **1b**) and are uniformly dispersed and uniform in size, having a particle size distribution, estimated from the TEM image, to be 3-5 nm.



Figure 1. (a)SEM images of Pt/ZrO2; (b)TEM images of Pt/ZrO2,

STEM EDX spectroscopy mapping confirmed the elemental distribution and composition of Pt/ZrO<sub>2</sub> and **Figure 2a** and **2b** displayed the typical HAADF-STEM image. Mapping images of platinum, zirconium, and oxygen (**Figure 2e, 2d** and **2f**) indicate that Pt is uniformly distributed on zirconia. The HRTEM image of

**Figure 2b** also demonstrates the successful synthesis of 7 wt% Pt/ZrO<sub>2</sub>. At the same time, it can be seen from **Figure 2b** that the lattice spacing (white) is approximately 1.96 nm, which corresponds to the (002) crystal plane of platinum.



Figure 2. HAADF-STEM images of: 7wt.% Pt/ZrO<sub>2</sub> (a,c), and STEM EDX spectroscopy mappings of: (d) Zr, (e) O, and (f) Pt; high-resolution TEM micrograph of: 5 wt.% Pt/ZrO<sub>2</sub> (b).

The crystal form and phase structure of the transition metal oxide (ZrO<sub>2</sub>) in the catalyst can be further determined by characterization of X-ray diffraction. Figure 3a and 3b clearly show the wide-angle and low-angle powder XRD patterns of the catalyst. The position of the diffraction peak shown is the same as the standard card value of ZrO<sub>2</sub> (space group Fm3m, PDF2 entry 49-1642). For the cubic ZrO<sub>2</sub> structure, three peaks at 30.12°, 50.22° and 59.74° 20 are attributed to the (111), (220) and (311) planes, respectively.<sup>[35, 36]</sup> In the obtained diffraction pattern (Figure 3a), the position of each diffraction peak was accurately obtained and confirmed to belong to a cubic zirconia structure (PDF 2 entry: 49-1642). However, at this calcination temperature, zirconia typically forms a monoclinic or tetragonal structure rather than a cubic structure. The reason for this phenomenon may be that the residual silicon oxide after the leaching treatment of Pt/ZrO<sub>2</sub> causes it to form a cubic structure. The specific surface area and pore size distribution of Pt/ZrO2 catalysts and SBA-15-OH were determined by BET and BJH models (Figures 3c and 3d). The nitrogen adsorption desorption isotherms indicate that both materials are mesoporous materials because they are all type IV curves as shown in Figure 4c. The unique capillary condensation phenomenon that occurs at P/P<sub>0</sub>=0.60-0.80 coincides with an ordered mesopores formed by removal of the silicon dioxide template. In addition, hysteresis loop appearing at higher pressures (P/P<sub>0</sub>=0.75-0.99) indicate the presence of structural defects or channels between the nanotubes.<sup>[35]</sup> Two peaks appear in the pore size distribution displayed in Figure 3d. The tube wall thickness of SBA-15-OH corresponds to a primary pore diameter centered in 3.5 nm, and the other peak comes from the inner hollow tube.

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**Figure 3. (a)** Wide-angle powder XRD (WXRD) patterns of Pt/ZrO<sub>2</sub>, compared with a standard ZrO<sub>2</sub> (space group  $Fm\overline{3}m$ , PDF2 entry 49-1642). Pt loading account is: 1, 3, 5, 7 and 9wt.%. **(b)** Low-angle powder XRD patterns of Pt/ZrO<sub>2</sub> nanotube arrays. **(c)** Nitrogen adsorption-desorption isotherms. **(d)** Pore size distributions of Pt/ZrO<sub>2</sub> and SBA-15-OH.

As shown in Figure S3, the chemical composition of the prepared catalyst and its elemental valence state were analyzed by XPS. The high-resolution XPS spectra of the 7%Pt/ZrO<sub>2</sub> Zr 3d and Pt 4f binding energies are shown in Figure S3a and Figure S3c, respectively. As the reported result, the Zr  $3d_{5/2}$ binding energy of stoichiometric ZrO2 is in the scope of 182.2-183.3 eV.  $^{\rm [37-40]}$  All Pt/ZrO\_2 catalysts displayed Pt  $4f_{5/2}$  peaks centered on 73.3 eV, 75.1 eV and 78.3eV (Figure S3c), which were corresponded to metallic Pt<sup>0</sup> and ionic Pt<sup>2+</sup> and Pt<sup>4+</sup> species, respectively.<sup>[36, 40, 41]</sup> The XPS data also confirmed the existence of the mixed valence states of Pt. As demonstrated in Figure S3b, three typical peaks were clearly observed in the O 1s XPS spectra of the Pt/ZrO2 catalysts. The binding energies in the range of 529.6-530.1eV and 531.7-532.1eV are attributed to to lattice oxygen (O<sub>latt</sub>) and adsorbed oxygen (O<sub>ads</sub>), respectively.[36]

# Preparation and characterization of $Pt/ZrO_2$ -GA and $Pt/ZrO_2$ -GA-MOF-5

Pt/ZrO2-GA was prepared via a boiling water bath method, and Pt/ZrO<sub>2</sub>-GA-MOF-5 was further prepared by a stepwise selfassembly method. The morphology and structure of the prepared Pt/ZrO<sub>2</sub>-GA and Pt/ZrO<sub>2</sub>-GA-MOF-5 were characterized by SEM and TEM (Figure 4a~4d). A representative SEM micrograph (Figure 4a) of Pt/ZrO2-GA shows a continuous macroporous structure that will improve ingress and egress of the catalyst and formaldehyde reactant. The corresponding TEM micrograph (Figure 4b), clearly shows that the Pt/ZrO<sub>2</sub> material is fixed on the graphene sheets having a size range of 400-600 nm. From the images of SEM and TEM, it can be confirmed that MOF-5 is formed on the Pt/ZrO2-GA surface by self-assembly. At the same time, the ultra-thin structure of the graphene sheet was observed, which proved its folding ability in a certain sense. In a word, the surface of Pt/ZrO<sub>2</sub>-GA was modified with a KH550 and succinic anhydride. Then, the Zn<sup>2+</sup> as a metal node is coordinated with the carboxylate-terminated Pt/ZrO2-GA, and finally, terephthalic acid is added as an organic ligand for self-assembly, and the growth process is repeated several times to obtain MOF-5. Herein, modifying the Pt/ZrO<sub>2</sub>-GA surface functional group is a critical step because of the formation of strong chemical bonding. Furthermore, by controlling the number of the self-assembly processes, the MOF crystallite size and number can be tailored. Figure 4c and 4d show the Pt/ZrO2-GA-MOF-5 catalyst, and there is an obvious MOF-5 growth on Pt/ZrO2-GA. The selfassembly reaction between Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and terephthalic acid resulted in MOF-5 crystals with an average size of 0.5-1 µm (Figure 4d)



**Figure 4.** SEM images of: (a) Pt/ZrO<sub>2</sub>-GA and (c) Pt/ZrO<sub>2</sub>-GA-MOF-5; TEM images of: (b) Pt/ZrO<sub>2</sub>-GA and (d) Pt/ZrO<sub>2</sub>-GA-MOF-5.

To confirm that the surface of Pt/ZrO<sub>2</sub>-GA was modified by MOF-5, XPS investigations were conducted, and the results shown in Figure S3d and Figure S2. The results confirmed the presence of zinc. Thermogravimetric analysis method was used to determine the thermostability of the catalyst and to quantify the loading of MOF-5 or other compositions on the catalyst. TGA measurements were performed under a N2 flow across a operation temperature from 25°C to 800°C and the results shown in Figure 5a. For all synthetic catalysts, the initial mass loss is typically associated with organic residues. The sharp peak appearing at ~486 °C is attributed to the decomposition of the MOF-5 organic ligand, indicating a complete collapse of the skeleton.<sup>[42]</sup> Further, from the results of TGA, it was calculated that the MOF-5 on the surface of the modified Pt/ZrO2-GA was ~5wt.%. Additionally, the IR spectra (Figure 5b) demonstrates the existence of MOF-5 in the catalyst. The asymmetric stretching of carboxylate groups of BDC (from the terephthalic acid) is shown in around 1501cm<sup>-1</sup> and 1588cm<sup>-1</sup>,<sup>[43, 44]</sup> and bands for the symmetric stretching of carboxylate groups were shown at 1438cm<sup>-1</sup> and 1379cm<sup>-1.[45]</sup> The IR spectrum of Pt/ZrO<sub>2</sub>-GA-MOF-5 showed several bands at 1300-660cm<sup>-1</sup>, which were derived from the out-of-plane vibrations of terephthalic acid.  $^{[46,\,47]}$  In Figure 5b, all the characteristic bands

10.1002/chem.201904426





Figure 5. (a) thermogravimetric analysis of MOF-5, 7wt.% Pt/ZrO<sub>2</sub>-GA-MOF-5 and 7wt.% Pt/ZrO<sub>2</sub>-GA across a temperature range of 25–800°C; (b) IR spectra of the catalyst and MOF-5 at 298 K.

# Catalytic performance of $Pt/ZrO_2$ -GA-MOF-5 toward HCHO Oxidation

All samples showed high catalysis activity for HCHO oxidation, even at reaction temperatures below 150°C, the conversion was still above 95%. 7wt.% Pt/ZrO2 showed the highest activity due to the optimal Pt loading. At the same time, too high a loading (9wt.% Pt) accounts to a decrease in catalytic efficiency. One of the reasons is that excessive loading causes agglomeration of Pt NPs, resulting in a decrease in specific surface area, thereby reducing the catalytic effect. As can be seen from Figure 6, the MOF supported catalyst increased the reaction rate of HCHO. As shown in Figure S6, the stability of 7wt. % of Pt/ZrO<sub>2</sub>-GA-MOF-5 was also investigated. Though undergo 24 hours of continuous catalytic reaction at 100°C, its catalytic efficiency remains above 99% and can not find any significant change in SEM images and XRD patterns. This result demonstrates the stability of the catalyst in this working environment.



**Figure 6. (a)** Relationship between formaldehyde conversion rate and reaction temperature; **(b)** XRD patterns of Pt/ZrO<sub>2</sub>-GA-MOF-5 (before and after reaction) and MOF-5; SEM micrographs of Pt/ZrO<sub>2</sub>-GA-MOF-5 (before reaction) **(c)** and (after reaction) **(d)**.

The SEM micrograph of the catalyst sample after being subjected to continuous reaction for 24 hours at 150°C with a HCHO flow rate of 20ml/min is shown in **Figure 6d**. The morphology of the spent catalyst was not observed to change significantly when compared with the morphology of the fresh catalyst (**Figure 6c**). To further demonstrate the durability of the catalyst, XRD analysis was performed. As shown in the **Figure 6b**, the XRD pattern of the catalyst before and after the reaction showed few change, indicating that it had good stability.<sup>[42]</sup> Furthermore, the MOF-5 diffraction pattern indicates that MOF-5 is stable during the continuous completely oxidation of HCHO and was successfully loaded onto the aerogel surface.

Thus, GAs provides good support for the catalyst during the catalytic reaction and provides excellent flow channels for the ingress and egress of gas molecules. At the same time, MOF-5 adsorbing HCHO on the surface of GA accelerates the reaction rate by enriching formaldehyde on the surface of the catalyst. A simplistic schematic diagram of the catalytic HCHO oxidation process on a Pt-supported ZrO<sub>2</sub> catalyst, is shown in Figure 7. The catalytic reaction process is divided into the following steps: First, Pt supported on zirconia adsorbs free oxygen and splits it into active O atoms. The formation of a hydrogen bond between the oxygen atom on the HCHO and the hydrogen atom in the hydroxyl group on the surface of the zirconia causes the carbon atom in the formaldehyde molecule to be positively charged, forming an electrophilic carbon atom. The electrophilic carbon atoms are then readily attacked by reactive oxygen atoms to form a surface dioxymethylene group which is then further oxidized to the formate salt. The formate formed on the surface of the catalyst is easily decomposed into adsorbed carbon monoxide and H<sub>2</sub>O. Therefore, the adsorbed carbon monoxide, formate and diformaldehyde are the most important intermediates in the catalytic reaction. Finally, CO is oxidized to  $CO_2$  by  $O_2$  and the reaction process ends. Oxidation of formic acid to carbon monoxide is the rate determining step of the reaction.<sup>[41, 43]</sup> Finally, a virtuous cycle of HCHO adsorption and catalytic oxidation is produced.



Figure 7. Reaction scheme of the catalytic oxidation of HCHO on Ptsupported  $ZrO_2$  catalysts.

# concentrated nitric acid (65 wt%) and 40 ml of $H_2O_2$ , refluxed at 80 $^\circ$ C for 3 hours, and filtered to give SBA-15-QH.^{[35]}

#### Preparation of Graphite Oxide (GO)

A certain amount of graphite sheet (1.5 g) was dispersed in a mixture of  $H_2SO_4/H_3PO_4$  (9:1 volume ratio), and then a strong oxidizing agent KMnO<sub>4</sub> (9.0 g) was slowly added to the above mixture under vigorous stirring, and the whole reaction system was in ice-water bath and ensured that the temperature is below 40°C. After the reaction was completed, the mixture was allowed to stand overnight. Next, after cooling to room temperature, the reaction mixture was poured into ice (~200cm<sup>3</sup>). Then, 30%H<sub>2</sub>O<sub>2</sub> was slowly added until the color of the solution turned bright yellow. After that, the mixture was allowed to stand overnight. Then, the precipitate therein was separated and washed. Subsequently, impurity ions in the product are removed by dialysis, and the process continues for one week. Then, graphene oxide is obtained by a freeze-drying method.

#### Preparation of Pt/ZrO2

Generally, a certain amount of chloroplatinic acid solution (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 1g/100ml, 1.878 g of zirconium oxychloride was impregnated with a certain amount of the above solution to adjust different Pt loadings. 1%, 1.91ml; 3%, 5.72ml; 5%, 9.53ml ; 7%, 13.34 ml; 9%, 17.15 ml), 2.00 g of SBA-15-OH, 3 ml of HCl (1.07 mol/L) were uniformly mixed and placed in the reaction kettle. The temperature was kept at 50° C for 24 h, and then heated to 90°C for 48 h. The obtained product was calcined in a tube furnace, air atmosphere, heating rate 1°C/min, calcined at 450°C for 6 h, and cooled down to ambient temperature naturally. In order to remove the SBA-15-OH template, the obtained product was uniformly mixed with a sodium hydroxide solution (2 mol/L), and refluxed at 70°C for 12 hours, and the operation was repeated twice with 35 ml of a sodium hydroxide solution each time. After the reaction, it was washed with ultrapure water until neutral, and the product was dried under vacuum at 60°C for 8 hours.

#### Preparation of Pt/ZrO2-GA

Take 50mg GO, ultrasonically disperse it in 10ml H2O and add a certain amount of catalyst (10mg, 20mg, 30mg), disperse evenly, then add 100mg L-ascorbic acid, dissolve completely, in 100°C water bath The reaction was carried out for 30 minutes, and then directly frozen at -40 °C for 1 hour. The water bath was again taken out at 100°C for 8 hours. After the reaction was completed, the excess water in the container was sucked out with a pipette, and finally freeze-dried.

#### Preparation of Pt/ZrO2-GA-MOF-5

The surface of Pt/ZrO<sub>2</sub>/GA was modified with succinic anhydride and KH550 (3-aminopropyltriethoxysilane). The carboxylation reaction of the prepared Pt/ZrO<sub>2</sub>/GA is first carried out. The aerogel was immersed in 1 ml KH550 solution (KH550: ethanol =1:10, volume ratio) and placed on a shaker for 8 hours. Then Pt/ZrO<sub>2</sub>/GA was immersed in 0.50 g of succinic anhydride/10 ml of DMF and placed on a shaker for another 8 hours. After the reaction is completed, it is rinsed several times with DMF. In order to modify the MOF on the surface of the aerogel, we prepared two solutions in advance for use. First, take 0.51g of terephthalic acid, 0.85ml of triethylamine. 40ml of DMF, and mix the three to form a solution: secondly, take 1.70g of zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), 50ml of DMF into a solution. Pt/ZrO<sub>2</sub>/GA was first soaked in 10 ml of zinc acetate solution, placed on a shaker for 30 mins; washed several times with DMF, then soaked in 10 ml of terephthalic acid solution, and placed on a shaker for 2 hours. This process alternates 4 times. The DMF in the aerogel was then replaced with absolute ethanol and finally lyophilized to give the final product.

Catalytic oxidation of HCHO

## Conclusions

Pt/ZrO<sub>2</sub>-GA-MOF-5 was prepared via a one-step, selfassembly method and was investigated as a catalyst toward the catalytic oxidation of HCHO. The Pt/ZrO2-GA surface was modified with MOF-5, as the latter is known to adsorb formaldehyde. At the same time, the GA network provides a highly accessible tortuous channel system for the ingress and egress of reactant and product molecules. The 7wt.% Pt/ZrO2 sample exhibited excellent catalytic performance, which was further improved after loading onto the aerogel by modification of the aerogel surface. This catalyst sample achieves ~100% formaldehyde conversion at low reaction temperatures (~100 °C). At the same time, the composite material demonstrated excellent stability during the catalytic oxidation of formaldehyde, maintaining performance after 24 hours of continuous reaction. As a result of the excellent catalytic performance and stability, the catalyst demonstrates great potential for a wide-range of applications.

## **Experimental Section**

#### Materials and Reagents.

The reagents and chemicals listed below can be used directly without any treatment. EO20PO70EO20 (P123) was purchased from Sigma-Aldrich. Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), tetraethyl orthosilicate (TEOs), L-ascorbic acid, 1,4-dicarboxybenzene, succinic anhydride, potassium permanganate was purchased from TOKYO CHEMICAL INDUSTRY CO.,LTD. Zirconyl chloride octahydrate (ZrOCl<sub>2</sub>·8H<sub>2</sub>O), KH550(3-aminopropyltriethoxysilane, APTES) was purchased from Shanghai Macklin Biochemical C.,Ltd. Graphite flake, sodium hydroxide, hydrochloric acid, nitric acid, hydrogen peroxide, absolute ethyl alcohol, N,N-dimethylformamide (DMF), zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) was purchased from Sinopharm Chemical ReagtenCo., Ltd. (China). Formaldehyde were purchased from Messer Air Liquide, Ltd. (China).

#### Characterizations.

SEM and TEM images were received by Hitachi S-4700 and FEI Tecnai G-20 microscopes, respectively. High resolution TEM images were obtained by FEI Tecnai F-20. The crystal phase was analyzed by X-ray diffraction (XRD) (X'Pert-Pro MPD) and high resolution TEM (HRTEM). The elemental composition of Pt/ZrO<sub>2</sub>-GA-MOF-5 was determined by XPS (ESCALAB 250Xi) and energy dispersive X-ray (EDX) spectroscopy, which was obtained by FEI Tecnai F-20 microscope. The stability and composition of Pt/ZrO<sub>2</sub>, Pt/ZrO<sub>2</sub>-GA, MOF-5 and Pt/ZrO<sub>2</sub>-GA-MOF-5 were analyzed by TGA (TG209 F1 Libra). The test for catalytic degradation performance was carried out in a fixed bed reactor. The concentration of HCHO was analyzed in real time by a formaldehyde detector (formaldehyde meter, PPM-400 ST).

#### Preparation of SBA-15-OH

130 ml of ultrapure water and 20 ml of concentrated hydrochloric acid (37 wt.%) were mixed to make dilute hydrochloric acid, 4.00 g of P123 was added and stirring was continued to completely dissolve in dilute hydrochloric acid, and then 8.320 g of TEOS was slowly added dropwise. And stirring at 38°C for 24 hours; then the mixture was hydrothermally reacted at 110°C for 24 hours. After the reaction was completed, the mixture was suction filtered to obtain a precipitate, which was dried at 80°C. The dried precipitate was slowly added to a mixture of 120 ml of

A temperature controlled fixed bed reactor containing a U-shaped quartz tube was used to catalyze the oxidation of HCHO. Typically, 50 mg of catalyst (in terms of Pt/ZrO<sub>2</sub>) was placed in the reactor, then one end was passed through HCHO (20 ml/min, 50 ppm, balanced in air) and the other end was connected to an exhaust collection bag. The concentration of HCHO was measured once every 10°C rise in temperature. The concentration of HCHO was analyzed using a formaldehyde detector (formaldehyde meter, PPM-400st).The HCHO conversion rate is calculated by equation (1):

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$
 (1)

 $\mathsf{C}_0$  and  $\mathsf{C}$  are the initial and measured concentrations of HCHO, respectively.

#### Acknowledgements

We gratefully acknowledge the financial support provided by the National Key R&D Program of China (2017YFC0210901, 2017YFC0210906), National Natural Science Foundation of China (51573122, 21722607, 21776190), Natural Science Foundation of the Jiangsu Higher Education Institutions of China (17KJA430014, 17KJA150009), the Science and Technology Program for Social Development of Jiangsu (BE2015637) and the project supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

**Keywords:** platinum • zirconia • aerogel • SBA-15-OH • formaldehyde oxidation • MOF-5

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A Pt/ZrO<sub>2</sub>-GA was prepared as a catalyst that can absorb and catalytically oxidize HCHO at low temperature. The MOF-5 was used to modify the surface of the catalyst and enhanced its adsorbability.In addition, the pores of graphene aerogel (GA)-supported material that facilitate diffusion of gas molecules and increase reaction rate.

MOF-5 нсно \$-H<sub>2</sub>O

CO<sub>2</sub> -0 со



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### Page No. – Page No.

Platinum-supported zirconia nanotube arrays supported on graphene aerogels modified with metal-organic frameworks: adsorption and oxidation of formaldehyde room at temperature