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Article

N-doped ordered mesoporous carbon as a multifunctional support of ultrafine Pt nanoparticles for hydrogenation of nitroarenes

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ARTICLE INFO

Article history:

Received 27 February 2017

Accepted 6 April 2017

Published 5 July 2017

Keywords:

N-doped mesoporous carbon

Multifunctional support

Ultrafine platinum nanoparticle

Hydrogenation reaction

Halogenated nitrobenzene

ABSTRACT

Due to the advantages of high surface areas, large pore volumes and pore sizes, abundant nitrogen content that favored the metal-support interactions, N-doped ordered mesoporous carbons are regarded as a kind of fascinating and potential support for the synthesis of effective supported catalysts. Here, a N-doped ordered mesoporous carbon with a high N content (9.58 wt%), high surface area (417 m²/g), and three-dimensional cubic structure was synthesized successfully and used as an effective support for immobilizing Pt nanoparticles (NPs). The positive effects of nitrogen on the metal particle size enabled ultrasmall Pt NPs (about 1.0 ± 0.5 nm) to be obtained. Moreover, most of the Pt NPs are homogeneously dispersed in the mesoporous channels. However, using the ordered mesoporous carbon without nitrogen as support, the particles were larger (4.4 ± 1.7 nm) and many Pt NPs were distributed on the external surface, demonstrating the important role of the nitrogen species. The obtained N-doped ordered mesoporous material supported catalyst showed excellent catalytic activity (conversion 100%) and selectivity (>99%) in the hydrogenation of halogenated nitrobenzenes under mild conditions. These values are much higher than those achieved using a commercial Pt/C catalyst (conversion 89% and selectivity 90%). This outstanding catalytic performance can be attributed to the synergetic effects of the mesoporous structure, N-functionalized support, and stabilized ultrasmall Pt NPs. Moreover, such supported catalyst also showed excellent catalytic performance in the hydrogenation of other halogenated nitrobenzenes and nitroarenes. In addition, the stability of the multifunctional catalyst was excellent and it could be reused more than 10 times without significant losses of activity and selectivity. Our results conclusively show that a N-doped carbon support enable the formation of ultrafine metal NPs and improve the reaction activity and selectivity.

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1. Introduction

Precious-metal nanoparticle (NP) catalysts play a vital role in fine chemical production, petroleum refining, and other sectors of the modern chemical industry [1,2]. The active metal

phase is always dispersed on a suitable support such as metal oxides (e.g., Al₂O₃ [3], ZrO₂ [4], and TiO₂ [5]), zeolites [6], and carbons [7,8] to enhance the activity and stability of the catalyst. The support type or properties such as acid-base and redox properties [9] can affect the formation of metal NPs or

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This work was supported by the National Natural Science Foundation of China (201573136, U1510105) and the Scientific Research Start-up Funds of Shanxi University (RSC723).

DOI: 10.1016/S1872-2067(17)62833-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 7, July 2017

metal-support interactions [10,11]; this affects the activity and stability of the solid catalyst, and therefore selection of an appropriate support is one of the most important factors to be considered in the design and synthesis of effective supported catalysts. Among various supports, carbon materials are one of the most common host materials for metal NPs [12,13] because of the wide availability of carbon sources [14–16] and their excellent wettability by organic compounds [17]. Various carbon-based catalysts have been developed, e.g., Pd/C [18,19], Pt/C [20,21], and Ru/C [22]. However, because of the weak interactions between the metal NPs and the carbon surface, it is difficult to control and maintain the size of the deposited noble-metal particles during the catalytic process, and NPs are prone to leach from the support [23]. The chemical and catalytic properties of traditional carbons therefore do not meet the high standards required for catalysis.

Recently, N-doped ordered mesoporous carbons (NOMCs) have emerged as important materials with various advantages [24–28]. The nitrogen atoms incorporated in the carbon architecture can not only change the physicochemical and electronic properties of the support, but also serve as basic or coordination sites that favor metal-support interactions and thereby stabilize small metal NPs [29]. Previous studies have suggested that nitrogen functional groups influence the nucleation and growth kinetics during catalyst NP deposition [30], resulting in smaller catalyst particles and increased dispersion [31]. This is useful because decreasing and controlling the supported metal NP size can significantly increase their surface: bulk atomic ratio. This can affect the total energy and fundamental properties of the NPs and therefore their catalytic performance [29]. Increased interactions (such as coordination and electron transfer) between small metal NPs and nitrogen-functionalized supports can reduce the mobility of the catalytic metal and prevent aggregation or sintering, leading to enhanced durability and stability [9,29]. Moreover, it has been shown that nitro-

gen groups in carbon materials can modify the electronic structure of catalyst NPs or serve as bifunctional groups to activate specific substrates, which might enhance the intrinsic catalytic activity [32]. Additionally, compared with amorphous supports, ordered mesoporous carbons with high surface areas, and large pore volumes and pore sizes facilitate mass transfer, and give a confinement effect, which further prevents metal NP growth. These effects all improve the catalytic efficiency [33,34]. NOMC matrixes are therefore ideal alternative catalyst supports for loading metal NPs. Much research has led to the use of NOMCs as supports for NP catalysts for efficient hydrogenation [35,36], oxidation [37,38], coupling [39], and hydrochlorination reactions [40]. However, there are few reports of the synthesis of highly ordered mesoporous carbon materials with high nitrogen contents using simple methods, and their use as catalyst supports [26,29,41]. The development of element-doped mesoporous carbons and their corresponding supported small NP catalysts is therefore still needed. Catalysts with more specific properties are also needed.

In this work, we used a NOMC as a support for a Pt-based solid catalyst. The NOMC was synthesized by a soft-templating method using 3-aminophenol as both the nitrogen and carbon source and F127 [poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer, EO₁₀₆PO₇₀EO₁₀₆] as a template (Fig. 1). Polymerization and successive carbonization steps at high temperatures gave a carbon material with a mesoporous structure and high content of nitrogen functional groups. In situ doping with nitrogen using nitrogen-containing precursors gives homogeneous incorporation of nitrogen into carbons, making such materials excellent model supports for exploring the impact of N-doping on the activities and stabilities of Pt-based catalysts. The effects of the NOMC support on the Pt NPs were investigated, and the catalytic activity and selectivity in the hydrogenation of halogenated nitrobenzenes were compared with those for a commercial Pt/C catalyst and

Fig. 1. Schematic diagram of formation of N-doped ordered mesoporous carbon supported catalyst, Pt/NOMC.

the corresponding nitrogen-free ordered mesoporous carbon (OMC) catalyst, Pt/OMC. Finally, to gain a fundamental understanding of the impact of N-doping on the durability of carbon support materials, recycling tests were performed to evaluate the overall stability of the material.

2. Experimental

2.1. Materials

All chemicals were used as received unless otherwise stated. Pluronic F127 was purchased from Sigma Aldrich. 3-aminophenol, phenol, formaldehyde (37 wt%) and hexamethylenetetramine (HMT) were purchased from the Shanghai Chemical Reagent Company of the Chinese Medicine Group. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, a commercial Pt/C (5 wt%) catalyst, and halogenated nitrobenzenes and other nitroarenes were purchased from the Aladdin Reagent Company.

2.2. Synthesis of NOMC support

The NOMC support was synthesized using a previously reported soft-templating method [26]. 3-Aminophenol (0.654 g) and HMT (0.42 g) were dissolved in water (75 mL) under vigorous stirring. Pluronic F127 (0.47 g) dissolved in water (5 mL) was added. The mixture was stirred at 35 °C for 24 h; the color of the solution changed from colorless to saffron yellow. The solution was aged at 95 °C under static conditions for 8 h. The solid product was recovered by filtration, washed with deionized water, and air-dried at 50 °C under vacuum overnight. The obtained polymer was carbonized at 600 °C for 3 h in a N_2 atmosphere at a heating rate of 1 °C/min to give the NOMC support.

A nitrogen-free OMC was prepared using a solvent-evaporation-induced aggregate assembly approach. In a typical procedure, 20 wt% NaOH aqueous solution (0.13 g) was added to melted phenol (0.61 g) at 42 °C in a flask under stirring for 10 min. Formalin (37 wt% formaldehyde, 1.05 g) was added. The mixture was stirred for 1 h at 70 °C and then cooled to room temperature. The pH was adjusted to 7.0 using HCl solution. Water was removed by vacuum evaporation and ethanol was added to form a 20 wt% ethanolic solution. An ethanolic resol solution (5.0 g) and tetraethyl orthosilicate (2.08 g) were added to a mixture of ethanol (8.0 g), HCl solution (0.2 mol/L, 1.0 g), and Pluronic F127 (1.6 g). The mixture was stirred at 40 °C for 2 h and transferred to a dish to allow ethanol evaporation at room temperature for 24 h. Thermopolymerization was performed at 100 °C for 24 h. Calcination was performed in a tubular furnace at 350 °C for 2 h and 900 °C for 2 h under a N_2 flow to give a mesoporous carbon-silica nanocomposite. The carbon-silica nanocomposite was immersed in 10 wt% HF solution for 24 h to remove the silica and give mesoporous carbon.

2.3. Immobilization of Pt NPs

An aqueous solution of the metal precursor was prepared

by dissolving $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.00 g) in water (100 mL) at room temperature. The prepared NOMC powder (0.282 g) was impregnated with H_2PtCl_6 solution (1.5 mL). After stirring for 2 h at room temperature, water was removed by rotary evaporation and the solid was dried in a vacuum at 50 °C. The solid was reduced in a 5% H_2 -95% N_2 mixed atmosphere at 200 °C for 2 h at a heating rate of 1 °C/min to give the solid Pt/NOMC catalyst.

2.4. Characterization

Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2-TF30 electron microscope operated at an accelerating voltage of 300 kV. N_2 adsorption-desorption isotherms were recorded using an ASAP2020 volumetric adsorption analyzer. The surface area was calculated from the adsorption branch in the relative pressure range 0.05–0.15 using the Brunauer-Emmett-Teller (BET) equation. The total pore volume was calculated at a relative pressure of $p/p_0 > 0.99$. Pore size distribution curves were obtained by analysis of the adsorption branch of the isotherm. X-ray diffraction (XRD) patterns were obtained using a desktop powder X-ray diffractometer at 40 kV and 30 mA with $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra Dld spectrometer, with an $\text{Al K}\alpha$ radiation (1486.6 eV) incident beam in a N_2 atmosphere.

2.5. Hydrogenation of nitroarenes

In a typical procedure, a halogenated nitrobenzene (2.56 mmol) and ethanol (5 mL) were added to a test tube containing the desired amount of Pt/NOMC (25 mg, 2.56 μmol Pt). The test tube was transferred to a stainless-steel autoclave and the autoclave was sealed. After purging several times with H_2 , the pressure was adjusted to 1 MPa and the system was stirred at 25 °C in a constant-temperature bath. After the reaction, the H_2 pressure was released and the solid catalyst was separated by centrifugation. The conversion and selectivity were determined by gas chromatography using an HP-5 capillary column (30 m $\times$ 0.32 mm $\times$ 0.5 μm). In the recycling tests, the solid catalyst obtained by centrifugation was added to fresh substrate and solvent, and directly used to perform the next catalytic cycle.

3. Results and discussion

The ordered mesoporous properties of the synthesized N-doped carbon support and corresponding solid Pt/NOMC catalyst were investigated using TEM. Fig. 2(a) and (b) show that the NOMC sample had a high degree of periodicity viewed from different directions. The low-angle XRD pattern of NOMC shows an intense peak corresponding to the (110) reflection along with weak shoulder peaks assigned to the (200) and (211) reflections (Fig. 2(e)). These results suggest that an ordered mesoporous support with cubic $\text{Im}\bar{3}\text{m}$ symmetry was obtained [26,42]. The XRD pattern after immobilization of Pt NPs, i.e., of the solid catalyst Pt/NOMC, is similar to that of the support, indicating that the periodic mesoporous structure was retained after Pt NP loading. TEM was used to determine the

Fig. 2. (a, b) TEM images of NOMC; (c) TEM image of Pt/NOMC (inset shows Pt particle size distribution); (d) Partial magnification of Pt/NOMC; (e) XRD patterns of NOMC and Pt/NOMC; N₂ adsorption-desorption isotherms (f) and (g) Pore size distributions of NOMC and Pt/NOMC.

size distribution of the supported Pt NPs on the NOMC; almost no Pt NPs were observed on the external surface of the support (Fig. 2(c) and (d)), possibly because the Pt NPs were mainly loaded into the channels of the mesoporous carbon. The images show that ultrasmall and uniform Pt NPs were homogeneously dispersed on the surfaces of the NOMC pores. The particle size distribution of the Pt NPs is shown in the inset in Fig. 2(c); the mean particle diameter was about 1.0 ± 0.5 nm. The well-dispersed ultra-small Pt NPs, without aggregation, can be attributed to the stabilizing effect of the incorporated nitrogen and the confinement effect of the ordered mesoporous structure.

The N₂ adsorption isotherms of NOMC and Pt/NOMC are type IV with a type-H2 hysteresis loop, indicating a mesoporous structure and spherical pores with narrow pore windows (Fig. 2(f)). This result is consistent with the TEM and XRD results. The isotherm shape was preserved after Pt NP loading, indicating that the Pt NPs did not block or alter the pore system. It is worth noting that the adsorption and desorption branches are not closed, a phenomenon that is often observed for porous polymers and sometimes for porous carbons, and which is not yet fully understood [26]. The BET surface area and total pore volume of the NOMC support were calculated to be 418 m²/g and 0.22 cm³/g, respectively, which might be beneficial for metal particle dispersion and fast diffusion of substrates and products during the catalytic process. After Pt NP loading, the specific surface area (344 m²/g) and pore volume (0.18 cm³/g) decreased slightly; this might be related to Pt loading in the mesochannels. The pore size of Pt/NOMC (Fig. 2(g)) differed only slightly from that of NOMC, suggesting that

the ordered mesostructure was well preserved after Pt NP loading, and the Pt/NOMC mesostructure was not blocked by Pt NPs.

XPS was used to investigate the interactions between the small Pt NPs and the nitrogen-functionalized support. Fig. 3(a) shows that the NOMC gave strong signals from carbon, nitrogen, and oxygen elements. The N 1s XPS spectrum shows two peaks; the lower energy peak, at 398.58 eV, can be assigned to pyridinic nitrogen, and the peak centered at 400.76 eV is attributed to pyrrolic nitrogen (Fig. 3(b)) [26]. Elemental analysis based on sample combustion showed that the bulk nitrogen content of the NOMC support was about 9.58 wt%. The Pt XPS spectrum of Pt/NOMC shows a doublet corresponding to Pt⁰ 4f_{7/2} (71.41 eV) and 4f_{5/2} (74.91 eV). The weak peaks at 72.52 and 76.8 eV correspond to Pt²⁺ species, and no peaks from Pt⁴⁺ were observed, which suggests that all the Pt⁴⁺ precursor had been reduced in situ by treatment with H₂ (Fig. 3(c)). The XPS data suggest that metallic Pt⁰ was the major phase formed on the catalyst surface (~76%). Notably, the binding energy of Pt⁰ 4f_{7/2} in Pt/OMC, i.e., without incorporated nitrogen, differs from the corresponding value for Pt/NOMC (71.41 versus 71.82 eV). This slight deviation could be related to weak interactions between the catalyst and the support.

p-Chloroaniline is an industrially important organic intermediate used in the synthesis of fine chemicals and pharmaceuticals [7]. The direct hydrogenation of halogenated nitrobenzenes is an attractive route for the formation of *p*-chloroaniline. However, hydrodehalogenation often occurs as a side reaction during the catalytic process, resulting in low catalytic selectivity. The development of functional catalysts

Fig. 3. XPS analysis of NOMC, Pt/NOMC, and Pt/OMC. (a) XPS survey; (b) N 1s; and (c) Pt 4f.

with specific properties that enable control of the catalytic activity and selectivity is therefore important. Solid catalysts that have both high activity and selectivity are highly desirable. In this study, we selected the hydrogenation of halogenated nitrobenzenes as a model reaction for evaluating our solid catalyst, i.e., Pt/NOMC, which has a high surface area, high nitrogen content, and ultrasmall Pt NPs.

The reaction was performed with ethanol as the solvent under mild conditions (25 °C, 10 bar H₂). Fig. 4(a) shows the catalytic kinetic curve for the hydrogenation of *p*-chloronitrobenzene over Pt/NOMC. Clearly, Pt/NOMC efficiently catalyzed hydrogenation and the conversion increased smoothly with reaction time. The reactant was fully converted in 0.5 h, and the selectivity for *p*-chloroaniline (99%) was high. These results are encouraging because hydrodehalogenation reactions were almost completely avoided. The relationship between conversion and the reaction time was almost linear, indicating that the hydrogenation was zero order. The turnover frequency (TOF) calculated from the kinetic plot (Fig. 4(a)) was high, i.e., 2508 h⁻¹. The Pt/NOMC properties suggest that the high activity and selectivity of the supported solid catalyst could be related to its high surface area, nitrogen functional groups, and ultrasmall NPs.

The performance of the Pt/NOMC catalyst was compared with those of other types of catalyst, i.e., Pt/OMC, a commercial Pt/C catalyst, and metal-oxide-supported catalysts (Pt/SiO₂ and Pt/TiO₂), in the hydrogenation of *p*-chloronitrobenzene under the same reaction conditions. The Pt loadings of the supported catalysts were all about 2 wt% (except in the case of the commercial Pt/C catalyst, which was 5 wt%), similar to the loading on the Pt/NOMC catalyst. The particle sizes and distributions differ depending on the support, therefore these solid catalysts were characterized using TEM. Fig. 4(c) shows that without the stabilizing effect of doped nitrogen functionalities, many Pt NPs were distributed on the external surface of the ordered mesoporous carbon but not inside the channels, and the particles were larger (4.4 ± 1.7 nm). These results indicate that the nitrogen species incorporated into the carbon support play a key role in preventing uncontrolled growth of the Pt NPs and stabilize the Pt NPs formed mainly inside the mesoporous channels. The catalytic activity of Pt/OMC in the hydrogenation of *p*-chloronitrobenzene was similar to that of Pt/NOMC, and 100% conversion was achieved in the same reaction time (Fig. 4(b)). However, the catalytic selectivity was a little lower (97.3% vs 99%), possibly because of the weak interactions between Pt and the NOMC support, shown by the XPS results.

Fig. 4. (a) Kinetic profile of hydrogenation of *p*-chloronitrobenzene over Pt/NOMC; (b) Catalytic performances of various types of catalyst; and TEM images of Pt/OMC (c), Pt/C (d), Pt/SiO₂ (e), and Pt/TiO₂ (f).

For the commercial Pt/C catalyst, only 89% conversion and 90% selectivity were achieved under similar reaction conditions. The higher activities of Pt/NOMC and Pt/OMC can be attributed to the ordered mesoporous structure, which could promote homogeneous distribution of Pt NPs and facilitate mass transfer. The activity of the Pt/SiO₂ catalyst, which is a commonly used solid catalyst, was low (conversion 46% and selectivity 93%). The low catalytic activity might be related to its poor oil wettability compared with those of other carbon supports. Furthermore, the particles were much larger than those on the other supported catalysts (Fig. 4(e)). The Pt/TiO₂ catalyst had small particles (Fig. 4(f)) and full conversion was achieved, but the selectivity was only 91%. These results show that the NOMC performed better than other common supports, especially in terms of reaction selectivity.

Leaching of metal NPs from supports and the growth of metal NPs during reactions are major problems for supported ultrasmall metal NP catalysts, and lead to a sharp decrease in the catalytic activity. The stability of Pt/NOMC was investigated by performing recycling tests in the hydrogenation of *p*-chloronitrobenzene. Fig. 5(a) shows that the solid catalyst was easily recovered by simple centrifugation and reused more

than 10 times without loss of catalytic activity and selectivity. The Pt concentration in the liquid reaction solution, determined using inductively coupled plasma atomic emission spectroscopy, was less than 0.1 ppm, indicating that Pt leaching into the liquid phase was negligible. The Pt/NOMC catalyst recovered after the 10th run was examined using TEM (Fig. 5(c)). There were no obvious differences between fresh Pt/NOMC and the recycled catalyst, although Fig. 5(d) shows that the particle size had increased slightly (1.0 ± 0.5 nm vs 2.0 ± 1.5 nm). The recyclability of Pt/OMC was also investigated for comparison (Fig. 5(b)). The conversion decreased with increasing cycle number. After 10 cycles, the conversion and selectivity had decreased to 57% and 88%, respectively. These results confirm that the interactions between small Pt NPs and the NOMC functional support are crucial in maintaining the activity and acting as an inhibitor during recycling.

Based on the superior performance of the NOMC-supported catalyst, the reactions of other halogenated nitrobenzenes and nitroarenes were investigated. The data in Table 1 shows that *o*-chloronitrobenzene and *m*-chloronitrobenzene were fully converted, without hydrodehalogenation reactions, under the test conditions (99.5% and 98.8% selectivity, respectively, entries 1 and 2). *p*-Bromonitrobenzene also reacted smoothly to give the corresponding amine with 95.5% selectivity (entry 3). Other nitrobenzene compounds with various substituent groups, i.e., hydroxy, methoxy, formyl, and ester groups, were also investigated. Excellent catalytic activities were achieved with *p*-nitrophenol, *o*-nitrophenol, *p*-nitroanisole, and methyl 4-nitrobenzoate as substrates, and >99% selectivities were achieved under the reaction conditions (entries 4–7). However, with 4-nitrobenzaldehyde and 4-nitrobenzyl alcohol as substrates, the selectivities were lower (85.4% and 70.0%, entries 8 and 9) because side reactions occurred more easily.

Fig. 5. Reusability of Pt/NOMC (a) and Pt/OMC (b); TEM image (c) and particle size distribution (d) of Pt/NOMC after recycling 10 times.

Table 1

Hydrogenations of nitroarenes with various substituents.

Entry	Substituent	Time (h)	Conversion (%)	Selectivity (%)
1		0.5	100	99.5
2		0.5	100	98.8
3		0.5	100	95.5
4		2	100	100
5		2	100	99.2
6		2	100	100
7		2	100	100
8		2	100	85.4
9		2	100	70

Reaction conditions: Pt/NOMC 25 mg, 2.56 mmol substrate, 1 MPa H₂, ethanol 5 mL, 800 r/min, 25 °C.

4. Conclusions

A N-doped ordered mesoporous carbon material with a high nitrogen content (9.58 wt%) was successfully prepared using a soft-templating method. Ultrasmall Pt NPs were uniformly distributed on the nitrogen-functionalized support to give a Pt/NOMC catalyst. The N-doped carbon gave well-dispersed and stable small NPs, and enhanced catalytic hydrogenation activity and selectivity compared with those of conventional supports, namely Pt/OMC, commercial Pt/C, and metal-oxide-supported catalysts (Pt/SiO₂ and Pt/TiO₂). The Pt/NOMC catalyst showed good stability and was reused 10 times without loss of catalytic activity.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 1252–1260 doi: 10.1016/S1872-2067(17)62833-X

N-doped ordered mesoporous carbon as a multifunctional support of ultrafine Pt nanoparticles for hydrogenation of nitroarenesJifen Liang, Xiaoming Zhang, Lingyan Jing, Hengquan Yang *
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N-doped ordered mesoporous carbon supported ultra-small Pt nanoparticles were successfully synthesized and used as an efficient solid catalyst in the hydrogenation of nitroarenes.

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氮掺杂有序介孔碳负载超小尺寸铂纳米颗粒催化硝基苯类化合物选择加氢

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摘要: 氮掺杂有序介孔碳材料不仅具有高的比表面积、大的孔容和均一可调的孔径等优点, 其骨架中丰富的氮原子还可以对材料的物理化学性质、配位金属电荷密度等进行调控, 是一类优异的催化剂载体。本文利用软模板(嵌段共聚物F127为模板), 以间氨基苯酚为碳源和氮前体, 制备出较高含氮量(9.58 wt%)和比表面积(417 m²/g), 以及规则孔径分布的介孔碳材料。结果表明, 制备的材料具有三维立方相结构。

以该碳材料作为载体, 使用传统浸渍氢气还原的策略负载纳米铂颗粒。发现氮掺杂的载体能够有效控制金属纳米颗粒的尺寸, 可实现超小尺寸Pt纳米颗粒的有效负载(1.0 ± 0.5 nm), 且纳米颗粒均匀分布于介孔碳材料的孔道中。

相比而言, 使用相同负载方法的情况下, 以不掺氮的介孔碳材料为载体, 纳米粒子的尺寸较难控制(4.4 ± 1.7 nm)且会发生孔道外颗粒聚集的情况。研究表明, 骨架中的氮原子与金属间弱的相互作用对纳米粒子有稳定作用。这对制备超小尺寸的金属纳米粒子催化剂具有一定的指导意义。此外, 由于纳米粒子的尺寸将大大影响催化剂活性中心的暴露程度, 进而影响催化剂活性。因此, 我们以硝基苯类化合物的氢化反应来评价该催化剂的催化性能。在室温和1 MPa H₂的温和条件下, 氮掺杂的介孔碳负载催化剂表现出了优异的催化性能。反应0.5 h, 对氯硝基苯可完全转化, 且选择性高达99%。相比而言, 商业化的Pt/C催化剂上反应的转化率和选择性分别为89%和90%。其它传统催化剂的比较, 如Pt/SiO₂, Pt/TiO₂, 同样表明, 氮掺杂介孔碳负载的催化剂具有更优异的催化性能。在相同反应条件下, Pt/SiO₂催化剂只能得到46%的转化率和93%的选择性, 而Pt/TiO₂催化剂虽然能够实现完全转化, 但选择性也仅为91%。由此可见, 氮掺杂的负载催化剂可大大提高反应活性和选择性, 能有效抑制脱氮现象的发生。这种高的催化性能可能与催化剂的介孔结构、氮功能化载体以及超小尺寸的Pt纳米

粒子的稳定有关。由于氮原子和介孔孔道的限域作用,氮掺杂介孔碳负载的催化剂也具有较好的催化稳定性,循环使用10次后,催化活性和选择性几乎没有下降。结果表明,循环使用后的催化剂金属粒子尺寸变化不大,进一步表明氮掺杂介孔碳载体对金属纳米颗粒的稳定作用。

关键词: 氮掺杂介孔碳材料; 多功能载体; 超小铂纳米颗粒; 加氢反应; 卤代硝基苯

收稿日期: 2017-02-27. 接受日期: 2017-04-06. 出版日期: 2017-07-05.

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基金来源: 国家自然科学基金(201573136, U1510105); 山西大学人才事业启动经费(RSC723).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).