DOI: 10.1002/cctc.201300377



Palladium Supported Catalysts for Nitrocyclohexane Hydrogenation to Cyclohexanone Oxime with High Selectivity

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Different kinds of activated carbon- and carbon nanotube-supported palladium catalysts were investigated in the selective hydrogenation of nitrocyclohexane to cyclohexanone oxime under mild conditions. Carbon nanotube-supported palladium catalysts demonstrate better catalytic performance than activated carbon-supported palladium catalysts in general because of their mesoporous structures, which are favorable supports for the accessibility of the reactants to the active sites and the product desorption from the catalyst. Hydrogen chemisorption, transmission electron microscopy and X-ray photoelec-

Introduction

Cyclohexanone oxime (CHO) can be used to produce ε -caprolactam, which is an important precursor for the manufacture of nylon-6 and plastics. The current commercial production of cyclohexanone oxime is mainly based on cyclohexane oxidation and cyclohexanone (CHE) ammoximation, as demonstrated previously.^[1,2] Of these synthetic processes, cyclohexane oxidation is a less efficient process, with per pass yield of 4-5% without a catalyst and 8-10% with cobalt catalysts.^[3] Moreover, this commercial process for the production of cyclohexanone oxime could produce a large amount of ammonium sulfate as a byproduct.^[4-7] Therefore, many researchers have tried to develop new methods for the production of cyclohexanone oxime. Raja et al. have developed a process for the production of cyclohexanone oxime and ϵ -caprolactam from cyclohexanone with use of bifunctional heterogeneous nanoporous aluminophosphate catalysts.^[8] However, the starting material is still cyclohexanone, which is obtained from cyclohexane oxidation. An alternative promising method for the production of cyclohexanone oxime is the nitrocyclohexane (NCH) hydrogenation process developed by DuPont.^[5,9] However, this process catalyzed by a supported palladium catalyst in the presence of

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http://dx.doi.org/10.1002/cctc.201300377.

tron spectroscopy indicate that higher composition of Pd⁺ on the catalyst surface, larger palladium surface area, and better palladium dispersion contribute to an increase in the activity and selectivity toward cyclohexanone oxime. In addition, single-wall carbon nanotube-supported palladium catalysts give the best result of 97.7% conversion of nitrocyclohexane and 97.4% selectivity toward cyclohexanone oxime. On the basis of the results of GC-MS and the designed experiments, a possible reaction scheme was proposed.

lead(II) oxide with approximately 70% yield of cyclohexanone oxime requires high pressure and environmentally unfriendly lead(II) oxide salts. Recent progresses in nitration technology have made it possible to obtain nitrocyclohexane with high selectivity and yield, which promotes the research interest in the hydrogenation of nitrocyclohexane to cyclohexanone oxime.^[10,11] Serna et al. have developed a sodium-doped Pt/ TiO₂ catalyst for the hydrogenation of nitrocyclohexane, with a cyclohexanone oxime yield of 80.3% at a selectivity of 84.5% and a nitrocyclohexane conversion of 95% at 4.0 MPa and 383 K.^[12] Au/Al₂O₃ has been investigated by Shimizu et al. in the selective hydrogenation of nitrocyclohexane, and the catalyst with smaller size gold particles demonstrates a high cyclohexanone oxime yield (86%) at 0.6 MPa and 373 K.^[13]

Carbon nanotubes (CNTs) have been widely used as supports for heterogeneous catalytic reactions since their discovery in 1991.^[14-17] They are suitable for both gas phase and liquid phase reactions and could be easily separated from the products; moreover, they can efficiently suppress the occurrence of side reactions.^[18-20] It has been proposed that CNTs could be favorable supports for palladium in liquid phase reactions after a suitable treatment, which is due to their efficient improvement in critical mass transfer on their large external surface area.^[21,22] Furthermore, they can boost the selectivity of the desired reactions.^[23] Our research group used Pd/CNTs as catalysts for the hydrogenation of nitrocyclohexane to cyclohexanone oxime, which gives a nitrocyclohexane conversion of 97.6% and a cyclohexanone oxime selectivity of 85.9% under mild conditions of 0.2 MPa and 323 K^[24]; however, this is still unsatisfactory. Herein, we report the preparation and characterization of several different types of CNT- and activated carbon (AC)-supported palladium catalysts and study the effects of different supports on the physical properties of the catalysts and their catalytic performance in the selective hydrogenation of nitrocyclohexane to cyclohexanone oxime.

Results and Discussion

Characterization of the catalysts

The palladium loading dose of Pd/MWCNTs-3, Pd/SWCNTs, and Pd/LAC catalysts (for details on these catalysts, see the Experimental Section) determined by using atomic absorption spectrometry (AAS) was 4.82, 4.80, and 4.78%, respectively. After the Pd/SWCNT catalyst was used four times, its palladium loading dose was 4.24%.

The BET surface area, pore diameter, and pore volume of different types of AC- and CNT-supported palladium catalysts are summarized in Table 1. It can be observed that the pore diam-

| Table 1. Textural properties of different catalysts. | | | | | | |
|--|---|-----------------------|---|--|--|--|
| Catalyst | Surface area [m ² g ⁻¹] | Pore diameter [nm] | Pore volume [cm ³ g ⁻¹] | | | |
| Pd/LAC | 240.3 | 0.96 | 0.21 | | | |
| Pd/CAC | 363.8 | 0.95 | 0.30 | | | |
| Pd/CSAC | 187.9 | 1.09 | 0.11 | | | |
| Pd/MWCNTs-1 | 102.7 | 2.44 | 0.56 | | | |
| Pd/MWCNTs-2 | 81.8 | 2.71 | 0.31 | | | |
| Pd/MWCNTs-3 | 71.9 | 2.43 | 0.73 | | | |
| Pd/SWCNTs | 277.6 | 2.73 | 0.60 | | | |
| Pd/DWCNTs | 257.3 | 2.73 | 0.55 | | | |

eters of the three AC-supported palladium catalysts are between 0.95 and 1.09 nm, which is the microporous structure range. Of these three catalysts, the Pd/CAC catalyst has the largest surface area of 363.8 m²g⁻¹ and pore volume of 0.3 cm³g⁻¹. CNT-supported palladium catalysts belong to the mesoporous structure range and have larger pore volume (0.31–0.73 cm³g⁻¹) and pore diameter (2.43–2.73 nm) than ACsupported palladium catalysts.

This can also be confirmed through Barrett-Joyner-Halenda (BJH) pore size distributions and nitrogen adsorption-desorption isotherms (Figure 1) of Pd/MWCNTs-3, Pd/SWCNT, and Pd/ LAC catalysts. The Pd/LAC catalyst (Figure 1c) shows an adsorption isotherm of type I, which indicates the capillary condensation of nitrogen within the uniform microporous structure. The isotherms of Pd/MWCNTs-3 (Figure 1a) and Pd/ SWCNTs (Figure 1 b) are of type III, which indicates that nitrogen covers the entire surface and no microholes exist in the CNT supports; moreover, the interaction between the supports and palladium plays the dominant role. Of the five types of CNT-supported palladium catalysts, Pd/SMCNTs and Pd/ DWCNTs have much large surface areas (277.6 and 257.3 m²g⁻¹) than those of multiwall CNT-supported palladium catalysts. Furthermore, the surface areas of all multiwall CNTsupported palladium catalysts are smaller than those of ACsupported palladium catalysts. The textural properties of the



Figure 1. N₂ adsorption–desorption isotherms and BJH pore size distributions of a) Pd/MWCNTs-3 (\bullet), b) Pd/SWCNTs (\bullet), and c) Pd/LAC (\blacktriangle).

supports have a great effect on their catalytic performance. The surface channels of the AC are easy to block because of their microporous pore size, which leads to the low content of active sites on the surface. However, the surface channels of CNTs could not be blocked easily because of their mesoporous pore size.^[25,26] The catalytic tests reveal that all CNT-supported palladium catalysts demonstrate better catalytic performance than AC-supported palladium catalysts. Thus, the support with larger pore diameter and pore volume may have a positive effect on the hydrogenation of nitrocyclohexane to cyclohexanone oxime.

The XRD patterns of Pd/LAC and five types of CNT-supported palladium catalysts are shown in Figure 2. The crystalline diffraction peak appearing at $2\theta = 26^{\circ}$ in the XRD patterns is



Figure 2. XRD patterns of a) Pd/LAC, b) Pd/MWCNTs-1, c) Pd/MWCNTs-2, d) Pd/MWCNTs-3, e) Pd/SWCNTs, and f) Pd/DWCNTs: C (●), Na (▲), Pd (■).

ascribed to carbon; the peaks at $2\theta = 32$, 45, and 57° are ascribed to sodium; and the peaks at $2\theta = 40$ and 47° are ascribed to palladium. The diffraction peak of carbon at $2\theta = 26^{\circ}$ (Figure 2a) is unclear in Pd/LAC, and there are distinct diffrac-

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tion peaks of carbon in Pd/MWCNTs-1 (Figure 2b), Pd/ MWCNTs-2 (Figure 2c), and Pd/MWCNTs-3 (Figure 2d). However, the diffraction peaks of carbon at $2\theta = 26^{\circ}$ are weak in Pd/ SWCNTs (Figure 2 e) and Pd/DWCNTs (Figure 2 f), which indicates that the carbon crystal particles are well dispersed. The characteristic diffraction peaks of palladium are different in Pd/ LAC and CNT-supported palladium catalysts. There are no clear diffraction peaks of palladium in the Pd/LAC catalyst, which indicates the existence of well-dispersed palladium phases. Two relatively clear diffraction peaks of palladium at $2\theta = 40$ and 47° appear in Pd/SWCNTs and Pd/DWCNTs, and only one diffraction peak of palladium at $2\theta = 40^{\circ}$ is detected in three multiwall CNT-supported palladium catalysts. Thus, the different types of supports have effects on the morphology, structure, and dispersion of crystalline palladium, which further affects their catalytic performance in the hydrogenation of nitrocyclohexane.

The TEM images of Pd/LAC and different types of CNT-supported palladium catalysts are shown in Figure 3. The surface structures of the prepared catalysts have diverse forms owing to their different supports. Pd/MWCNTs-1 (Figure 3b), Pd/ MWCNTs-2 (Figure 3 c1 and c2), and Pd/MWCNTs-3 (Figure 3 d1 and d2) catalysts consist of graphite planes in a fishbone stacking arrangement. The parallel graphite layer can be observed in Pd/SWCNTs (Figure 3 e) and Pd/DWCNTs (Figure 3 f). The structures of the supports have a great effect on the size, morphology, and crystal of the active component. Under the same preparation conditions of the catalysts, the statistical analysis data reveal that the palladium particle size is approximately 2.9-5.1 nm in Pd/LAC; approximately 2.2-4.4 nm in Pd/ MWCNTs-1, Pd/MWCNTs-2, and Pd/MWCNTs-3; and approximately 2.0-3.0 nm in Pd/SWCNTs and Pd/DWCNTs; the last one is smaller than others. The palladium particles are in the shape of circle or regular polygon and are embedded within the supports.

The hydrogen chemisorption data of different catalysts are summarized in Table 2. It can be observed that CNT-supported palladium catalysts demonstrate better dispersion, larger hydrogen uptake quantity, and larger metallic surface areas than AC-supported palladium catalysts. Of the different CNT-supported palladium catalysts, Pd/SWCNTs demonstrate the best dispersion, the largest hydrogen uptake quantity, and the largest metallic surface area, which may favor the nitrocyclohexane hydrogenation process.

The chemical compositions of Pd/MWCNTs-3, Pd/DWCNTs, and Pd/SWCNTs were characterized by using X-ray photoelectron spectroscopy (XPS). The XPS core level spectra of Pd 3d of the above catalysts are shown in Figure 4. The Pd 3d spectra are composed of two peaks: the right peak around 335 eV is attributed to the Pd 3d_{5/2} spectral peak, and the left peak around 341 eV belongs to the Pd 3d_{3/2} spectral peak. The peaks around 335 and 337.6 eV are assigned to Pd⁰ and Pd²⁺, respectively. The binding energy peak of the core level and a narrowing of the valence band belonging to the bulk metal would be shifted.^[27-29] In highly dispersed samples, the shift in the core level binding energies can be 1.0–1.3 eV. Thus, another peak around 335.8 eV is presumed to belong to Pd⁺. The surface



compositions of Pd/SWCNTs, Pd/DWCNTs, and Pd/MWCNTs-3 are given in Table 3. It can be observed that Pd/SWCNTs have the highest content of Pd^+ on the catalyst surface.



Figure 3. TEM images of a) Pd/LAC, b) Pd/MWCNTs-1, c) Pd/MWCNTs-2, d) Pd/MWCNTs-3, e) Pd/SWCNTs, and f) Pd/DWCNTs.

| Table 2. Hydrogen chemisorption data for different catalysts. | | | | | | |
|---|--|---|-------------------|--|--|--|
| Catalyst | H ₂ uptake ^[a] [μLg ⁻¹] | Metallic SA ^[b] [m ² g ⁻¹] | Dispersion [%] | | | |
| Pd/SWCNTs | 63.6 | 120.7 | 27.1 | | | |
| Pd/MWCNTs-3 | 54.5 | 103.5 | 23.2 | | | |
| Pd/DWCNTs | 49.3 | 93.5 | 20.9 | | | |
| Pd/LAC | 42.8 | 81.2 | 18.2 | | | |
| [a] H ₂ uptake/cumulative quantity. [b] Metallic surface area. | | | | | | |



Figure 4. XPS Pd 3d spectra of a) Pd/MWCNTs-3, b) Pd/DWCNTs, and c) Pd/ SWCNTs.

| Table 3. Surface catalysts. | compositions of | three CNT-supported | palladium |
|-----------------------------|---------------------|---------------------|----------------------|
| Catalyst | Pd ⁰ [%] | Pd+ [%] | Pd ²⁺ [%] |
| Pd/SWCNTs | 29.7 | 39.0 | 31.3 |
| Pd/MWCNTs-3 | 47.5 | 31.1 | 21.5 |
| Pd/DWCNTs | 40.0 | 26.6 | 33.3 |

Catalytic tests

The results of the hydrogenation of nitrocyclohexane to cyclohexanone oxime catalyzed by eight supported catalysts are summarized in Table 4. In general, CNT-supported palladium catalysts demonstrate better catalytic performance toward cyclohexanone oxime than AC-supported palladium catalysts under the same preparation conditions of the catalysts and reaction conditions. On the basis of the pore diameter and pore volume data listed in Table 1, AC-supported palladium catalysts belong to the microporous structure range whereas CNT-supported palladium catalysts belong to the mesoporous structure range. The molecular sizes were estimated by using the Gaussian package, and all geometrical optimizations for the reactants, intermediates, and products were performed by using a DFT hybrid exchange-correlation energy density functional consisting of the Becke three-parameter exchange energy density functional and the Lee-Yang-Parr correlation functional.^[30-34] All calculations were performed at the DFT B3LYP/6-311 + G(d) level by using the Gaussian 03 package (version E02), with tight SCF convergence and ultrafine integration grids. The results show that the molecular sizes of the reactants of nitrocyclohexane is 0.65 nm and those of the reaction products of cyclohexanone oxime, cyclohexanol, cyclohexanone, cyclohexylamine, and cyclohexylhydroxylamine are 0.66, 0.69, 0.65, 0.68, and 0.68 nm, respectively. The presence of

| Catalyst | Conv. [%] | Conv. [%] | | Selectivity [%] | |
|--|-----------|-----------|------|-----------------|------|
| | NCH | СНО | CHA | CHL | CHE |
| Pd/LAC | 98.9 | 55.0 | 5.0 | 4.6 | 0.1 |
| Pd/CAC | 99.2 | 60.5 | 5.6 | 3.2 | 0.1 |
| Pd/CSAC | 91.0 | 38.9 | 4.6 | 2.9 | 0.1 |
| Pd/MWCNTs-1 | 99.8 | 64.2 | 11.5 | 2.4 | n.d. |
| Pd/MWCNTs-2 | 99.6 | 78.5 | 1.0 | 1.1 | n.d. |
| Pd/MWCNTs-3 | 99.9 | 87.9 | 3.4 | 4.6 | n.d. |
| Pd/DWCNTs | 98.1 | 83.5 | 0.2 | 4.5 | n.d. |
| Pd/SWCNTs | 97.3 | 94.6 | 0.3 | 2.9 | n.d. |
| Pd/SWCNTs ^[b] | 97.3 | 94.6 | 0.2 | 4.9 | n.d. |
| Pd/SWCNTs ^[c] | 97.8 | 91.4 | 0.7 | 3.7 | n.d. |
| Pd/SWCNTs ^[d] | 95.5 | 84.7 | 2.6 | 4.7 | 0.1 |
| [a] Reaction conditions: nitrocyclohexane 1.3 g; temperature 323 K; time 6 h; pressure 0.3 MPa; ethylenediamine 10 mL; NCH = nitrocyclohexane; | | | | | |
| CHO = cvclohexanone oxime: CHL = cvclohexanol: CHE = cvclohexanone: | | | | | |

a large fraction of micropores in the catalyst can partially block the accessibility of the reactants to the palladium sites.^[26] During the nitrocyclohexane hydrogenation process, the reactant nitrocyclohexane needs to be adsorbed onto the palladium site and the reaction product cyclohexanone oxime needs to leave the active sites in time to avoid further conversion to other products. Because the molecular sizes of these substances are close to the size of the micropores of AC-supported palladium catalysts, the pore diameter is unfavorable for their adsorption and diffusion. However, the pore diameter of CNTsupported palladium catalysts is three to four times larger than the molecular size of the reactants and products. This could be the reason why CNT-supported palladium catalysts demonstrate better catalytic performance than AC-supported palladium catalysts in general.

Of the five CNT-supported palladium catalysts, Pd/SWCNTs give the best result of nitrocyclohexane conversion of 97.3%, cyclohexanone oxime selectivity of 94.6%, and cyclohexanone oxime yield of up to 92.0% whereas Pd/MWCNTs-1 give a cyclohexanone oxime yield of just 64.1%. The catalyst support plays an important role in catalytic selectivity, and the same type of support with different morphology and structure could greatly affect the catalytic performance. On the basis of the characterization results of the catalysts, Pd/SWCNTs, Pd/DWCNTs, and Pd/MWCNTs-3 were compared and analyzed in detail. Of these three CNT-supported palladium catalysts and one of the ACsupported palladium catalysts (Pd/LAC), Pd/SWCNTs demonstrate the best catalytic performance, which are followed successively by Pd/MWCNTs-3, Pd/DWCNTs, and Pd/LAC. In addition to the reason of the microporous and mesoporous structures of the different kinds of catalyst supports, it can be observed from the hydrogen chemisorption data that Pd/SWCNTs show the largest hydrogen uptake quantity, the largest metallic surface areas, and the best dispersion of the active components, which are also followed successively by Pd/MWCNTs-3, Pd/DWCNTs, and Pd/LAC.

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The adsorption and reactivity of nitro compounds depend not only on the nature of the metal but also on the crystallite size and the way they interact with the support. $^{\scriptscriptstyle [35-37]}$ The MWCNTs, DWCNTs, and SWCNTs have different structures (Figure 3), and thus the supported palladium demonstrates different morphology, size, and metal-support interaction, which may affect the reduction state of palladium. The XPS results have confirmed that the surface composition of Pd⁺ in Pd/ SWCNTs is the highest, followed by that of Pd/MWCNTs and Pd/DWCNTs under the same reduction conditions. The results of the hydrogenation of nitrocyclohexane catalyzed by Pd/ DWCNTs, Pd/MWCNTs, and Pd/SWCNTs show that the selectivity toward cyclohexanone oxime increase from 83.5 to 87.9 and 94.6%, which indicates that the reduction state of palladium (Pd⁺) favors the formation of cyclohexanone oxime and decreases the complete hydrogenation to other products.

The proposed reaction scheme

On the basis of the results of GC-MS, it can be found that in addition to the main product cyclohexanone oxime, other products were also formed, such as cyclohexylamine, cyclohexanol, and cyclohexanone, along with an unstable intermediate cyclohexylhydroxylamine. The distribution of the products relies heavily on the catalyst and the large amount of the intermediate, and some extremely small amounts of unquantifiable products are observed with AC-supported palladium catalysts (Table 4). From a mechanistic point of view, several reaction steps are required to produce cyclohexylamine, cyclohexanone, and cyclohexanol from nitrocyclohexane and they were expected to appear as secondary products unless the intermediates react before desorbing from the catalyst surface.^[12] Cyclohexylamine could be produced through consecutive hydrogenation, with cyclohexylhydroxylamine as the intermediate.[38,39] However, cyclohexanone oxime was used as the raw material to proceed with the hydrogenation reaction and extremely small amounts of cyclohexylamine and cyclohexanol were observed. This was also confirmed. It was found that cyclohexanone oxime can be reduced with hydrogen in the presence of a metal-based catalyst, which forms either cyclohexylamine or cyclohexanone^[22,40-42] and cyclohexanol can be obtained through the hydrogenation of cyclohexanone. Furthermore, cyclohexylhydroxylamine was detected by using GC-MS. Taking into account the above discussion, we can propose a possible reaction scheme (Scheme 1) that can illustrate the nitrocyclohexane hydrogenation process.

Effect of the reaction conditions

We have investigated the effect of reaction time, temperature, and pressure on nitrocyclohexane hydrogenation catalyzed by Pd/SWCNTs (Figure 5). The effect of reaction time on the distribution of the products indicates that the yield of cyclohexanone oxime reaches the maximum value in 6 h and then decreases. The reaction temperature has a great effect on the selectivity toward cyclohexanone oxime. The conversion of nitrocyclohexane reaches 98% at 303 K, 0.3 MPa, 6 h, and the selectively toward the selectivity toward the selection temperature for the selectivity toward the selection temperature of the selectivity toward the selectivity



Scheme 1. A proposed reaction mechanism for the liquid phase hydrogenation of nitrocyclohexane.

tivity toward cyclohexanone oxime is only approximately 72% at such a low temperature; higher temperature is also not good for the selectivity toward cyclohexanone oxime. The effect of the reaction pressure also indicates that the yield of cyclohexanone oxime first increases and then decreases; it has the maximum value at 0.5 MPa. A comprehensive research on the reaction time, pressure, and reaction temperature gives the best result of nitrocyclohexane conversion of 97.7% and cyclohexanone oxime selectivity of 97.4%, and the yield of cyclohexanone oxime increases to 95.2%, which improves the results reported in the previous literature.

The results of the catalyst recycle reactions are also summarized in Table 4. After each reaction, the Pd/SWCNT catalyst was separated through filtration and then used for the next cycle. However, the catalytic performance has little changes in the second cycle. To explore the leaching of the metal particles during the recycle reactions, we separated the catalyst from the reaction solution and the results of AAS analysis demonstrate that the active component did not get lost in the solution. The palladium loading dose of the recycled catalyst was also tested by using AAS. After the Pd/SWCNT catalyst was used four times, its palladium loading dose was 4.24%. The reasons why the catalytic performance decreased may be that part of the active sites were covered with organic materials, rather than the metal leaching from the support.

Conclusions

Different kinds of activated carbon- and carbon nanotube (CNT)-supported palladium catalysts were prepared and characterized by using nitrogen adsorption-desorption, XRD, TEM, hydrogen chemisorption, X-ray photoelectron spectroscopy, and atomic absorption spectrometry. The effect of the support was investigated in the selective hydrogenation of nitrocyclohexane to cyclohexanone oxime on these supported palladium catalysts. The nitrogen adsorption-desorption and the calculation results indicate that the CNT support with a mesoporous structure is favorable for the accessibility of the reactants to the active sites and the product desorption from the catalyst. This could be the reason why CNT-supported catalysts demonstrate better catalytic performance than activated carbon-supported catalysts in general. The results of hydrogen chemisorp-



Figure 5. Effect of reaction time, temperature, and pressure on nitrocyclohexane hydrogenation. Conversion of nitrocyclohexane (\blacksquare), selectivity toward cyclohexanone oxime (\blacktriangledown), selectivity toward cyclohexanol (\blacktriangle), selectivity toward cyclohexylamine (\bullet).

tion, TEM, and X-ray photoelectron spectroscopy reveal that higher surface composition of Pd⁺, larger palladium surface area, and better palladium dispersion contribute to an increase in the activity and selectivity toward cyclohexanone oxime. In addition, the optimization results show that the yield of cyclohexanone oxime reaches 95.2% at a nitrocyclohexane conversion of 97.7% and cyclohexanone oxime selectivity of 97.4% with Pd/SWCNTs. On the basis of the results of GC–MS, the designed experiments, and the literature, a possible reaction scheme was proposed.

Experimental Section

Preparation of the catalysts

Three kinds of ACs and five kinds of different structure CNTs were purchased from Shenzhen Nanometer Gang Co., Ltd., and used as supports. The ACs made from lignin, coal, and coconut shell were labeled as LAC, CAC, and CSAC, respectively, and the five different structure CNTs were multiwall CNTs with different diameters and lengths, double-wall CNTs, and single-wall CNTs, which were labeled as MWCNTs-1, MWCNTs-2, and MWCNTs-3; DWCNTs; and SWCNTs, respectively. The following is an example to illustrate the catalyst preparation process by using one of these supports.

The CNTs were first treated with concentrated nitric acid (68 wt%) at 303 K for 12 h and then filtered and washed several times with distilled water until the pH reached 7; finally, the CNTs were dried in vacuum at 383 K for 12 h. The catalyst was prepared by using the incipient impregnation method. Palladium chloride (PdCl₂) was used as the precursor of the active component. First, PdCl₂ (0.2 g) was dissolved into a solution of distilled water (12 g) and concentrated hydrochloric acid (1.2 g, 38 wt%) under ultrasonication for 30 min. Then, the sodium hydroxide solution (10 wt%) was added into the above solution and the pretreated supports were impregnated in the solution at 303 K for 10 h under stirring. Finally, the mixture was dried in vacuum at 383 K for 12 h and calcined under flowing nitrogen at 473 K for 4 h. The catalysts were obtained after reduction under flowing hydrogen at 523 K for 3 h.

Characterization of the catalysts

Specific surface area, pore volume, and pore size distribution of the samples were determined by using a Quantachrome's NOVA 2200e automated gas sorption system. Specific surface areas and pore size distributions were calculated by using BET and BJH methods. The XRD data were collected by using a Rigaku D/Max 2550 VB+ 18 kW X-ray diffractometer under the conditions of 40 kV, 30 mA, CuK_{α} radiation, with a scanning rate of 1^o min⁻¹ in the range of $2\theta = 10-60^{\circ}$. The TEM measurements were determined by using a JEOL JEM-3010 microscope operating at 200 kV, which allowed recording of high-resolution electron microscopy images with a point-to-point resolution of 0.17 nm. The instrumental magnification ranged from 50 to 1500000, which was measured by using an Oxford Instruments' energy dispersive microanalysis system (energy resolution = 133 eV). The types and the amount of the metal state were analyzed by using a Kratos's AXIS Ultra DLD instrument (energy resolution = 0.48 eV, imaging space resolution = 3 μ m, and minimum analysis area = 15 μ m). Hydrogen chemisorption was measured by using a Quantachrome's ChemBET 3000 instrument. The catalyst was reduced previously at 523 K for 3 h in hydrogen stream, and the adsorbed hydrogen on the palladium surface was removed under the flowing nitrogen stream. The catalyst was subsequently cooled to ambient temperature under the nitrogen stream. The hydrogen pulses (0.02 mL) were injected until the eluted areas of consecutive pulses became constant. The amount of palladium atoms on the surface was calculated by assuming that hydrogen adsorption was stoichiometric. The surface area of palladium was calculated from the palladium atomic crosssectional area. AAS was performed by using an AA-7000 spectrophotometer (Shimadzu). The catalysts were pretreated as follows: First, all samples were calcined at 873 K for 12 h, and then the samples were added successively to formic acid (5 mL) and nitrohydrochloric acid (8 mL) and dried at 358 K for 2 h. The treated samples were dissolved in concentrated hydrochloric acid (20 mL) at 353 K and diluted by an appropriate amount of distilled water. The palladium content of the sample was determined at $\lambda = 247.6$ nm by using AAS, and the loading dose was obtained by using the standard curve method.

Typical reaction method

The liquid phase hydrogenation of nitrocyclohexane was performed in a 50 mL Teflon-lined stainless-steel autoclave with a magnetic stirrer. Typically, nitrocyclohexane, ethanediamine solvent, and the prepared catalyst were added to the reactor. The autoclave was sealed, purged with nitrogen, and then pressurized with H₂ and heated to the required temperature. Upon completion of the reaction, the catalysts were removed through filtration. The content of nitrocyclohexane and that of the products were determined by using GC (Agilent 7820A) equipped with a flame ionization detector and a 30m DB-1701 capillary column (JW Scientific) using naphthalene as the internal standard. Typical gas chromatograms are given in the Supporting Information.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21276218), the Program for New Century Excellent Talents in University (NCET-10-0168), the Specialized Research Fund for the Doctoral Program of Higher Education (20124301110007), and the Project of Hunan Science and Technology Bureau (2012FJ1001).

Keywords: cyclohexanone oxime • hydrogenation nanostructures • nitrocyclohexane • supported catalysts

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Received: May 17, 2013 Revised: June 9, 2013 Published online on July 24, 2013