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Article

High selectivity to *p*-chloroaniline in the hydrogenation of *p*-chloronitrobenzene on Ni modified carbon nitride catalyst

Teng Fu, Pei Hu, Tao Wang, Zhen Dong, Nianhua Xue, Luming Peng, Xuefeng Guo, Weiping Ding*

Key Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China

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ABSTRACT

A nanocomposite composed of Ni modified carbon nitride was synthesized and used in the hydrogenation of *p*-chloronitrobenzene. H/D exchange demonstrated that the hydrogen chemisorbed on the surface of this nanocomposite catalyst had a hydrogen atom density of 0.65/nm². It was active for hydrogenation but its activity was inferior to the hydrogen adsorbed on a Ni/Al₂O₃ catalyst. Catalytic tests showed that this catalyst possessed a lower activity than Ni/Al₂O₃ but the selectivity towards *p*-chloroaniline was above 99.9%. Even at high conversion, the catalyst maintained high selectivity, which was attributed to the unique surface property of the catalyst and the absence of a site for the adsorption of *p*-chloronitrobenzene, which prevents the C–Cl bond from breaking.

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1. Introduction

As an important chemical intermediate, *p*-chloroaniline (*p*-CAN) is widely used in the synthesis of herbicides, dyes, drugs, and pesticides [1,2]. Until now the best way to synthesize this compound is the direct hydrogenation of *p*-chloronitrobenzene (*p*-CNB) due to its low impact on the environment. The main obstacle to this reaction is the dehalogenation reaction which also occurs. Raney Ni is the most widely used catalyst in this reaction due to its high activity, but in order to maintain the selectivity of the reaction, inhibitors must be added into the reaction system [3]. Noble metals have also been applied in this reaction, but their selectivity is still far from satisfactory and the high cost of noble metals has prevented large scale application. In recent years nanotubular materials have been widely studied. Our previous report showed that noncrystalline NiPB nanotube can be used as a highly effective heterogeneous catalyst for this reaction [4]. Other methods to prevent the dehalogenation process include

modulating the interaction between the metal and the support [5–7] and using an alloy of different metals [8,9]. But it still is a challenge in the hydrogenation of *p*-CNB to *p*-CAN to achieve high selectivity at high conversion with a good catalyst.

As a unique metal-free polymer material, carbon nitride (CN) has been intensively studied in different areas due to its versatile chemical and physical properties [10–16]. Its unique electronic structure and outstanding chemical stability make it a promising candidate for applications in catalysis such as photocatalytic water splitting, oxygen reduction, and the selective conversion of organic functional groups [17–22]. CN has also been used for supporting noble metals [23–26] and as an energy storage material [27]. By different modification methods, the properties of CN can be tuned to make it suitable for different applications. For example, by doping heteroatoms such as S, P, B, and other functional groups into the structure of CN, its band structure and surface property can be modified [28–32] for the further improvement of CN. In our previous work, we encapsulated highly dispersed Ni on Al₂O₃ with CN. It

* Corresponding author. Tel: +86-25-83595077; Fax: +86-25-83686251; E-mail: dingwp@nju.edu.cn

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was demonstrated that in this catalyst, the Ni was reduced to its metallic state and by donating its electron to CN, a strong interaction was formed between the nickel and CN; the points of the catalyst are shown in Fig. 1. By this method, we successfully modified the electronic properties of CN and endowed it with the ability to adsorb and activate hydrogen [33]. In this work, we use this nanocomposite catalyst as an efficient heterogeneous catalyst for the hydrogenation of *p*-CNB to *p*-CAN. The catalyst showed very high selectivity (>99.9%) at high conversion (>95%).

2. Experimental

First, a synthesized nanostructured Al_2O_3 was employed as the support. The Al_2O_3 was prepared by a hydrothermal approach with an alumina sol as precursor, and then calcined in air at 823 K for 12 h. An aqueous solution of $\text{Ni}(\text{NO}_3)_2$ was impregnated onto the Al_2O_3 by incipient wetness impregnation, dried in air at 373 K for 12 h and finally calcined in air at 723 K for 4 h. The product was denoted as $\text{NiO}/\text{Al}_2\text{O}_3$. Before the catalytic test, the $\text{NiO}/\text{Al}_2\text{O}_3$ was reduced in 5 vol% H_2/N_2 atmosphere at 873 K for 6 h. The product was denoted as $\text{Ni}/\text{Al}_2\text{O}_3$. The nanocomposite catalyst was synthesized by adding 1 g $\text{NiO}/\text{Al}_2\text{O}_3$, 2 g ethylenediamine, and 4 g carbon tetrachloride into 80 mL *m*-xylene. The system was heated to 363 K and stirred for 4 h and then heated to 413 K and stirred for another 4 h. After that the dark brown solid mixture was dried in an oven for 12 h and then ground into a fine powder. Finally the composite was treated in N_2 (50 mL/min) at 873 K with a heating rate of 2 K/min and kept at these conditions for 6 h to carbonize the polymer. The product was denoted as $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$. The sample composed of CN and Al_2O_3 was synthesized by the same method using Al_2O_3 as the starting material.

X-ray diffraction (XRD) patterns were obtained on a Phillips X'Pro diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) at 40 kV and 25 mA. Fourier transform infrared (FT-IR) spectra of the samples were obtained on a Bruker Vertex 70 spectrophotometer using KBr pellets, recorded with 64 scans with a reso-

lution of 4 cm^{-1} . Transmission electron microscopy (TEM) measurements were conducted with a JEOL JEM-200CX instrument at an accelerating voltage of 200 kV. Thermogravimetric (TG) curves were taken on an STA 449C-Thermal Star 300 instrument (NETZSCH, Germany) in air with a heating rate of 10 K/min to 1073 K. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a commercial XPS system (PHI 5000 VersaProbe) equipped with a hemispherical electron analyzer and monochromatic $\text{Al K}\alpha$ X-ray exciting source. H/D exchange was conducted by the following steps. The catalyst sample (200 mg) was reduced in 5 vol% H_2/N_2 (30 mL/min) at a heating rate of 10 K/min to 423 K and kept at this temperature for 1 h. Then the sample was cooled in the same atmosphere to room temperature and the flow was switched to Ar (35 mL/min) to remove physical adsorbed H_2 . Deuterium exchanged for proton present on the sample was measured by increasing the temperature to 873 K at a heating rate of 10 K/min under 5 vol% D_2/Ar (30 mL/min). The signal of HD was monitored by mass spectrometry.

The hydrogenation reaction was carried out in a bath-type autoclave reactor. In a typical reaction, the catalyst (50 mg) and *p*-CNB (50 mg) were added into the $\text{C}_2\text{H}_5\text{OH}$ solvent (50 mL). Hydrogen was introduced into the reactor at room temperature to the pressure of 0.6, 0.8, 1.0, 1.2, or 1.4 MPa. The reactor was heated to the required temperature and kept at this temperature for 2 h. After the reaction, the reactor was cooled to room temperature naturally and the catalyst was filtered off. The resulting solution was analyzed by gas chromatography with a flame ionization detector using an HP-5 column.

3. Results and discussion

Figure 2(a) shows the XRD patterns of the samples. The characteristic peaks at 37.4° , 39.5° , 45.7° , and 67.2° can be attributed to the (311), (222), (400), and (522) planes of Al_2O_3 , respectively. All the samples showed the characteristic XRD peaks indexed to Al_2O_3 and there was no peak which can be attributed to nickel oxide, metal nickel or NiAl_2O_4 , which indicated that the nickel was highly dispersed. $\text{CN}/\text{Al}_2\text{O}_3$ and $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ did not show the typical (002) peak of CN. This was attributed to its relatively low intensity compared to that of Al_2O_3 . After the encapsulation of CN, Fig. 2(b) shows the TEM image of $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ after heating in N_2 . We can see the layered CN surrounding the surface of the catalyst with a thickness of 2–3 nm. This was consistent with TG results (Fig. 2(d)). Fig. 2(e) shows the schematic structure of the catalyst, which is similar to the structure in our previous work.

Figure 2(c) shows the FT-IR profiles of the samples with CN. $\text{CN}/\text{Al}_2\text{O}_3$ and $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ showed similar absorption peaks: the C–N stretching modes between 1120 and 1620 cm^{-1} and the N–H stretching vibration modes at 3440 cm^{-1} , which were ascribed to the CN surrounding the surface of the catalyst [34]. Fig. 2(d) shows the TG profiles of $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{CN}/\text{Al}_2\text{O}_3$. The amounts of CN in $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ and $\text{CN}/\text{Al}_2\text{O}_3$ were 22 wt% and 23 wt%, respectively, indicating that the CN content in the sample was not changed by the existence of Ni. The DSC profiles demonstrated that the CN in $\text{CN}/\text{Ni}/\text{Al}_2\text{O}_3$ started to de-

Fig. 1. Schematic showing the principle of the catalyst composed of nickel modified carbon nitride comprising (1) electron donation from nickel to CN, (2) dissociative adsorption of hydrogen on CN, and (3) highly selective reduction of *p*-CNB to *p*-CAN by the activated hydrogen.

Fig. 2. (a) XRD patterns of the samples; (b) TEM image of CN/Ni/Al₂O₃; (c) IR profiles of CN/Al₂O₃ and CN/Ni/Al₂O₃; (d) TG profiles of CN/Al₂O₃ and CN/Ni/Al₂O₃; (e) Schematic show of the structure of the catalyst based on the data of characterization.

Fig. 3. XPS spectra of CN/Ni/Al₂O₃. (a) C; (b) N; (c) Ni.

compose at a lower temperature as compared to the CN in CN/Al₂O₃. This feature demonstrated an interaction between the nickel and the CN.

Figure 3 shows the XPS spectra of the CN/Ni/Al₂O₃ catalyst.

The atomic ratios of the elements are shown in the figure and the remaining atomic proportion was attributed to Al and O in the catalyst. The C 1s core level spectrum revealed the appearance of two additional carbon components to the typical *sp*²

Fig. 4. H/D exchange profiles of CN/Ni/Al₂O₃ (a) and CN/Al₂O₃ (b).

Table 1

The catalytic performance of the catalysts for hydrogenation of *p*-CNB to *p*-CAN.

Entry	Catalyst	Time (h)	<i>p</i> -CNB conversion (%)	<i>p</i> -CAN selectivity (%)
1	Ni/Al ₂ O ₃	2	82.3	75.6
2	Ni/Al ₂ O ₃	4	100	63.1
3	CN/Al ₂ O ₃	2	0	—
4	CN/Al ₂ O ₃	4	0	—
5	CN/Ni/Al ₂ O ₃	2	31.2	>99.9
6	CN/Ni/Al ₂ O ₃	4	57.5	>99.9
7	CN/Ni/Al ₂ O ₃	10	96.8	>99.9

Reaction conditions: Catalyst 50 mg, *p*-CNB 50 mg, ethanol 50 mL, initial hydrogen pressure 1 MPa, 393 K.

hybridized graphitic carbon at 284.6 eV. The peak at 285.4 eV was attributed to carbon atoms covalently bonded with N atoms in an aromatic structure. The peak at 286.6 eV was attributed to the *sp*² hybridized carbon bonded to the –NH₂ group in the aromatic ring. The N 1s core level spectra can be deconvoluted into four peaks located at 398.5, 399.1, 400.2, and 401.1 eV, which were assigned to pyridinic nitrogen, amine nitrogen, pyrrol nitrogen, and graphitic nitrogen, respectively

[35,36]. The C/N ratio was 5.5, which was nearly the same as the result of the elemental analysis with a value of 5.8. The Ni 2*p*_{3/2} core level spectra comprised two peaks located at 855.1 and 856.8 eV, which were assigned to the Ni which has a strong interaction with the CN and alumina, thus keeping Ni itself in an electron deficient metal state.

Figure 4 shows the quantitative H/D exchange results of CN/Ni/Al₂O₃ and CN/Al₂O₃. For CN/Ni/Al₂O₃, the main peak α of HD evolution was at 516 K with an amount of 156 μmol/g. This exchange temperature was higher than that of Ni/Al₂O₃ in our previous report. This phenomenon probably indicated that the activity of the hydrogen chemisorbed on the surface of CN/Ni/Al₂O₃ was inferior to that on Ni/Al₂O₃. The β species at the higher temperature was attributed to the residual H in the CN matrix. The density of adsorbed H atom was 0.65/nm², and from the N content in the sample, the molar ratio of the chemisorbed H and N was 1/27. For the sample composed of CN encapsulated Al₂O₃, the peak temperature for H-D exchange was delayed to 770 K. The β species mainly represented hydrogen tightly bonded to the CN matrix, which is inert compared to the hydrogen chemisorbed on the surface of the Ni modified CN. The amount of this kind of hydrogen was more than 256 μmol/g. This observation demonstrated that the α species hydrogen adsorbed on the CN in CN/Ni/Al₂O₃ and then exchanged with deuterium at a rather mild temperature was the chemisorbed hydrogen active in the hydrogenation reaction.

Table 1 shows the hydrogenation of *p*-CNB catalyzed by the different samples. The Ni/Al₂O₃ catalyst possessed much higher activity than CN/Ni/Al₂O₃. After 4 h of reaction, the conversion of *p*-CNB over Ni/Al₂O₃ reached 100%, but the selectivity to *p*-CAN dropped from 75.6% to 63.1%. In contrast, the CN/Ni/Al₂O₃ catalyst possessed a relative low hydrogenation activity, but its selectivity towards *p*-CAN was very high (>99.9%). This can be attributed to the relatively low activity of the chemisorbed hydrogen on the catalyst surface shown in the H/D exchange. As the reaction time was increased to 10 h, the conversion of the *p*-CNB reached 96.8% while the selectivity towards *p*-CNB was kept above 99.9%. The CN/Al₂O₃ catalyst was completely inactive for the hydrogenation of *p*-CNB, indicating that the hydrogen in CN itself is a nonreactive hydrogen species.

Figure 5(a) shows the catalytic performance of CN/Ni/Al₂O₃

Fig. 5. Catalytic activity of CN/Ni/Al₂O₃ catalyst under different initial hydrogen pressures (a) and reaction temperatures (b).

Fig. 6. Catalytic activity of CN/Ni/Al₂O₃ at 393 K with an initial hydrogen pressure of 1 MPa (a) and reuse test of the catalyst (b).

under 393 K and different initial hydrogen pressure. As the hydrogen pressure increased, the conversion of *p*-CNB increased accordingly. But after the initial hydrogen pressure reached 1.4 MPa, the selectivity to *p*-CAN started to decrease. Figure 5(b) shows the catalytic activity of CN/Ni/Al₂O₃ at 1 MPa of initial H₂ pressure and different reaction temperatures. At 353 K the catalyst was almost inactive, and as the temperature increased, the conversion of *p*-CNB increased. When the temperature reached 413 K, the selectivity began to decrease and at 433 K the selectivity had dropped to 80.6%. We concluded that the catalyst possessed very high selectivity to *p*-CAN even at high reaction temperature and hydrogen pressure.

Figure 6 shows that as the conversion of *p*-CNB increased, the selectivity to *p*-CAN was maintained at nearly 100%, indicating that dehalogenation did not occur as the reaction proceeded. Moreover, the catalyst can be reused several times without activity loss. This result demonstrated that the catalyst possessed high stability under the reaction conditions.

4. Conclusions

A CN/Ni/Al₂O₃ catalyst was synthesized and applied in the hydrogenation of *p*-CNB to *p*-CAN. The catalyst showed very high selectivity to *p*-CAN. This was attributed to the relatively low activity of the chemisorbed hydrogen on the catalyst surface. Also, because the nickel surface was surrounded by CN, it lacked a site for the adsorption of *p*-CNB, which contributed to its high selectivity. This nanocomposite composed of Ni modified CN showed promise for application in selective hydrogenation reactions and other related processes under mild conditions.

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Graphical Abstract

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High selectivity to *p*-chloroaniline in the hydrogenation of *p*-chloronitrobenzene on Ni modified carbon nitride catalystTeng Fu, Pei Hu, Tao Wang, Zhen Dong, Nianhua Xue, Luming Peng, Xuefeng Guo, Weiping Ding*
Nanjing UniversityNickel modified carbon nitride used in the hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline exhibited very high selectivity at high conversion.

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J, gren H, Sundgren J E. *Thin Solid Films*, 2005, 471: 19[36] Arrigo R, Havecker M, Schlogl R, Su D S. *Chem Commun*, 2008: 4891**镍调节氮化碳催化剂用于对氯硝基苯高选择性还原至对氯苯胺**

符 滕, 胡 佩, 王 涛, 董 珍, 薛念华, 彭路明, 郭学峰, 丁维平*

南京大学化学化工学院, 介观化学教育部重点实验室, 江苏南京210093

摘要: 作为一种重要的化学中间体, 对氯苯胺广泛应用于杀虫剂、染料和医药等。考虑到对环境的影响, 目前合成对氯苯胺最为有效的方法仍然是对氯硝基苯的直接加氢过程。该反应的主要难点在于要做到严格的不脱氯, 即在反应过程中不能生成苯胺。传统上所采用的雷尼Ni催化剂虽然活性很高, 但对氯苯胺的选择性较低, 因此通常情况下需要向反应体系中加入抑制剂以提高产物选择性。贵金属也可用作催化剂, 但其选择性也不高, 且价格高昂。采用适当方法调节金属-载体间相互作用或使用不同金属的合金也可来提高反应的选择性。不过总体而言, 利用简易的催化剂在高转化率条件下获得高的对氯苯胺选择性依然是一个挑战。

氮化碳(CN)作为一种近年来被广泛研究的材料, 其结构主要由以 sp^2 共价键相连接的C和N原子构成, 因而具有很多独特多变的性质。它的电子性质容易受到与其接触材料性质的影响。当CN与不同材料相互接触时, 电子可以在二者之间相互转移。作为一种催化剂, CN在光解水和氧还原等多相催化反应中都表现出非常有趣的性质。这主要归因于其特殊的电子性质和结构性质, 例如其费米能级附近的态密度会随着N含量的增加而增加, 并形成一种类金属的材料。CN表面所拥有的丰富的缺陷位和N原子为电子的局域和锚定提供了位点, 因而它可能用作金属催化剂的载体, 而金属与CN之间形成的异质结已经被证明可以提高其光解水产氢的性能。研究表明, 当某些金属与CN发生接触时, 两者之间产生很强的相互作用, 从而为我们调控CN的性质提供了一种可能的途径。本课题组曾通过利用CN包裹高度分散于 Al_2O_3 表面的Ni, 发现在制备过程中催化剂中的Ni被还原到了金属态, 且与CN之间形成了电子相互作用, 从而成功地调节了CN的电子性质和能带结构。

本文将这种纳米复合材料用于对氯硝基苯加氢制备对氯苯胺反应中。结果发现, 催化剂中的Ni在与CN相互作用时将电子转移到CN上, 使得CN具备了吸附和活化氢的能力。氢氙交换实验发现, CN表面化学吸附氢的交换温度在516 K左右, 含量约为156 $\mu\text{mol/g}$, 氢的吸附密度约在0.65/ nm^2 。考虑到CN中的N含量, 化学吸附的H和N物种的比例约在1/27。当用于对氯硝基苯加氢反应时, 虽然该催化剂的活性相对较低, 但产物选择性很高, 对氯硝基苯转化率达到96.8%时, 对氯苯胺的选择性仍在99.9%以上。而对于Ni/ Al_2O_3 催化剂, 虽然其活性很高, 但对氯苯胺选择性却较低, 且随着对氯硝基苯转化率的增加, 体系中苯胺的含量逐渐上升, 表明本文所采用的催化剂具有独特的很高的产物选择性。这可能与其相对较弱的加氢活性以及催化剂表面被CN包裹, 缺乏可以吸附对氯硝基苯的金属位点有关。Ni调节的CN所构成的纳米复合材料有望用作选择加氢等一系列反应的温和催化剂。

关键词: 加氢反应; 对氯硝基苯; 氮化碳; 镍; 选择性

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*通讯联系人. 电话: (025)83595077; 传真: (025)83686251; 电子信箱: dingwp@nju.edu.cn

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