



Hydrogenation of nitrobenzene over a composite catalyst based on zeolite supported N-doped carbon nanotubes decorated with palladium

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Abstract

A catalyst nanocomposite was synthesized based on zeolite supported nitrogen-doped carbon nanotubes (N-CNT) decorated with palladium nanoparticles. Zeolite beads impregnated with nickel nitrate solution were used as CCVD catalyst support during the synthesis of N-CNT. Then the zeolite supported N-CNT was decorated with palladium nanoparticles and the final nanocomposite was tested in nitrobenzene hydrogenation. The structure of the nanocomposite was characterized by SEM. The surface of the zeolite beads is extensively covered by N-CNT. The particle size distribution of the palladium nanoparticles on the surface of N-CNT is relatively homogenous (< 7 nm). The catalytic activity of the nanocomposite was the highest at 10 bar and 323 K while the achieved nitrobenzene/aniline conversion was 99.9% after 4 h of hydrogenation.

Keywords N-CNT · Palladium · Hydrogenation · Nitrobenzene

Introduction

Nitrobenzene and aniline are two very important starting materials for the chemical industry (polymers, herbicides and pharmaceuticals). Aniline as the starting compound for 4,4'-methylenedianiline (MDA) and thus, 4,4'-methylene diphenyl diisocyanate (MDI) production, is essential for polyurethane manufacturing [1, 2]. Nowadays, aniline is synthesized from nitrobenzene using various catalysts. The

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most widely used catalysts in this procedure are catalytically active metals such as palladium, platinum and Raney nickel on different catalyst supports (monolith, activated carbon etc.) [3–7]. Carbon nanotubes (CNT) are excellent support materials for catalytically active metals owing to their high mechanical strength, chemical stability, large surface area and notable electronic interaction [8]. Different metals (Pd, Rh, Ir, Pt, Ru) on CNT supports were efficiently used as catalysts in selective hydrogenation processes for fuel-cell applications and biomass conversion [8–13]. The substrate conversion and the stereoselectivity is improved by applying CNT supports [8]. In the cases of nitrobenzene and nitrocyclohexane hydrogenation, catalytic activity was quite high when CNT supported platinum catalyst was used at atmospheric pressure and ambient temperature [14, 15]. Amino-, carboxyl- and, hydroxyl functionalized multiwalled carbon nanotube (MWCNT) based ruthenium catalysts were compared in sorbitol to glycol hydrogenolysis [16]. The most active catalyst was the nitrogen containing Ru/MWCNT sample [16]. Nitrogen-doped graphene and carbon nanotube (N-CNT) based composite catalysts were successfully applied in the electroreduction of oxygen and their activity was higher compare to the platinum/activated carbon system [17]. Nitrogen incorporation into the nanostructures could improve the chemical and electronic properties of the system and thus, promote the activation of the metal catalyst [18, 19]. Furthermore, the strength of the interaction (binding energy) between metal nanoparticles and CNT supports is also increased by the incorporation of nitrogen atoms [20]. The incorporation of nitrogen atoms can be achieved by using nitrogen containing carbon sources (e.g. butylamine) for the in situ nanotube synthesis [21]. For industrial applications, it is very important to use catalysts which can be handled easily and separated from the reaction medium. For this reason, the powder form of CNT supported catalysts are not suitable. The deposition of carbon nanotubes onto supports for example zeolite beads, alumina or ceramic based rings and saddles can be a good solution (supports on supports, SoS). Our aim was to study the applicability of such SoS system in hydrogenation. Palladium nanocomposite for catalytic purposes was synthesized based on zeolite supported nitrogen-doped carbon nanotubes. The first step was the N-CNT synthesis on the surface of zeolite beads and this complex SoS was decorated by palladium nanoparticles. The final nanocomposite catalyst was tested in hydrogenation (nitrobenzene/aniline conversion).

Materials and methods

Materials

The nitrogen-doped carbon nanotubes on the surface of zeolite beads were prepared with catalytic chemical vapor deposition (CCVD) method during which hydrocarbons in vapor state are decomposed in the presence of catalytically active metals. We used *n*-butylamine (*Charlau Chem.*) as a carbon precursor, while nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, *Merck Chem.*), zeolite beads (diam. 2 mm, 5 Å molecule sieve, *Roth*), and Patosolv mixture of aliphatic alcohols (*Molar*

Chem.) was used as precursors for the CCVD catalyst preparation. The palladium decorated zeolite/N-CNT supported catalyst was made by using anhydrous palladium(II) chloride (*Chinoin Ltd.*). Nitrogen and hydrogen (purity 4.0, *Messer*) was also used. The final palladium nanocomposite catalyst was tested in nitrobenzene (*Sigma Aldrich*) hydrogenation. To identify the products, analytical standards (*Dr. Ehrenstorfer*) such as aniline, nitrobenzene, nitrosobenzene and *N*-methylaniline were used.

Characterization methods

The morphology tests of N-CNT samples were carried out with a high resolution transmission electron microscope (HRTEM, FEI Technai G2, 200 kV) and a scanning electron microscope (SEM, Hitachi S 4800). All samples were drop casted onto 300 Mesh Copper grids (*Ted Pella Inc.*) from an aqueous suspension for HRTEM investigations. In the case of the SEM study, carbon tape rubber was used to prepare the samples. The palladium nanoparticles on the N-CNT/zeolite beads were characterized by SEM, while the outer diameters of the nanotubes were manually scaled using the ImageJ program [23]. Purity of CNTs were checked with thermogravimetric test (TG) applying a MOM Derivatograph-C device in an oxidative atmosphere using 5 K/min heating rate. The nitrogen incorporation types into the CNT were identified by X-ray photoelectron spectroscopy (XPS, SPECS spectroscopy with a Phoibos 150 MCD 9 analyzer). The morphology of the palladium nanoparticles was studied by HRTEM. Further characterization of the metal particles on the surface of the catalysts were carried out by XRD using a Bruker D8 Advance diffractometer. The hydrogenation of nitrobenzene was carried out in a Büchi Uster Picoclave reactor system (SI, Fig. S1). The hydrogenation tests were performed at three different pressure (5, 10, 20 bar), while the reaction temperature was set to 323 K and the mixing speed was 1000 min⁻¹. Sampling took place after starting the hydrogenation at 5, 10, 15, 20, 30, 40, 60, 80, 120, 180, 240 min.

The hydrogenation process was followed by using Agilent 7890A gas chromatograph coupled with Agilent 5975C Mass Selective detector. The separation was performed on RTX-624 column (60 m × 0.25 mm × 1.4 μm). The injected sample volume was 1 μL at 200:1 split ratio, while inlet temperature was set to 473 K. The carrier gas was helium with constant flow (2.28 mL min⁻¹), the oven temperature was set to 323 K for 3 min and it was heated up to 523 K with 10 K/min increments and kept there for another 3 min.

Synthesis of N-CNT-zeolite catalyst supports on supports (SoS) system

The N-CNT synthesis was carried out at 973 K by applying nitrogen atmosphere in a quartz-reactor, which was placed in a tube furnace. The liquid carbon source was butylamine, and zeolite beads impregnated with nickel-nitrate aqueous solution was used as catalyst. In aqueous solution, 0.25 g nickel(II) nitrate was added to the 5A zeolite and 1 h later, the aqueous phase was evaporated by rotary evaporator. Then, the beads were dried at 393 K overnight. The amine-containing carbon precursor

was precisely injected directly into the main furnace by using a syringe pump. It was immediately evaporated and transported into the reactor space with nitrogen carrier gas. The N_2 flow during the synthesis of N-CNT was set to 100 mL/min. The total mass of the beads was 50 g, while the butylamine was injected with a rate of 6 mL h^{-1} . No reductive pre-treatment was used on the catalyst before the CCVD process.

Decoration of zeolite bead supported N-CNT with palladium nanoparticles

Impregnation method was used to decorate the SoS (zeolite beads supported N-CNT) with palladium nanoparticles. During the impregnation, 0.10 g palladium(II) chloride was dissolved in a mixture of 50 mL distilled water and 1 mL hydrochloric acid. The zeolite beads supported carbon nanotubes were added to the prepared solution. The aqueous phase was evaporated by rotary evaporator and the system was dried at 393 K overnight. The heat treatment of the sample was carried out at 673 K, and then, the temperature was kept, and the sample was reduced in hydrogen flow (50 mL min^{-1}). The final catalytically active metal content of the prepared catalysts was 5 wt%.

Catalytic activity tests of the palladium nanocomposite (5% Pd/N-CNT-Zeolite)

The hydrogenation of nitrobenzene (in methanol) was used as a test system to study the catalytic activity of the final palladium nanocomposite. The concentration of nitrobenzene was 0.3 mol L^{-1} , while 2 g catalyst was added to the system. The reaction was carried out in a Büchi Uster Picoclave reactor system (SI, Fig. S1).

Results and discussion

Characterization of the palladium nanocomposite (5% Pd/N-CNT-Zeolite)

The prepared N-CNT/zeolite composite catalyst support (Fig. 1a) was studied by SEM, XPS and TGA methods. The presence of N-CNTs on the surface of the zeolite beads was proved by SEM. The dense carbon nanotube coverage of the zeolite beads can be seen on the SEM image (Fig. 1b).

The bond type of the incorporated nitrogen atoms was characterized by XPS (Fig. 1c). On the deconvoluted XPS spectra, the N 1s band was found at 398.4 eV, which indicates the presence of pyridinic nitrogen atoms. The peak of graphitic nitrogen was also identified at 410.1 eV. The oxidized forms of nitrogen were present in the samples which is indicated by a peak at 410.5 eV. The carbon nanotube content attached to the zeolite beads was measured with thermogravimetry (Fig. 1d). Based on the DTG curve the N-CNT content was up to 2.6 wt%. The weight loss below 623 K can be attributed to the dehydration of the sample.

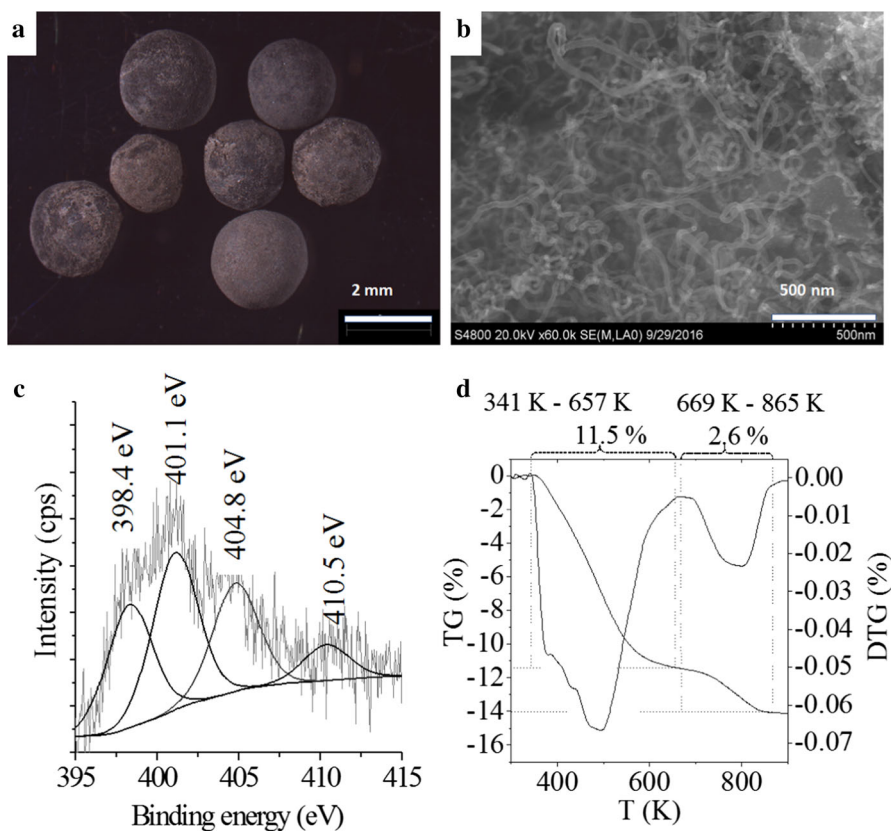


Fig. 1 Stereomicroscopic image of the system (a), SEM (Scanning Electron Microscope) image (b), XPS (X-ray photoelectron spectroscopy) spectra (c) and TG (thermogravimetric)-DTG (derivative thermogravimetric) curves (d) of the zeolite supported N-CNT (nitrogen-doped nanotubes)

Characterization of the palladium nanocomposite catalyst

The presence of metallic palladium phase was confirmed by XRD measurements (Fig. 2a). In the XRD pattern, the reflection of Pd(111) and Pd(200) planes can be observed at 40.1° and 44.1° 2θ , respectively. The reflection peak which belong to the carbon nanotube is present at 26° . Other reflections were also found, but those corresponds to the zeolite core. Based on the SEM picture of the Pd/N-CNT-zeolite, the palladium particles were highly dispersed and showed homogenous coverage on the nanotube layer (Fig. 2b). The majority of the Pd particles has a diameter of < 5 nm while the average is 2.9 nm (Fig. 2c). On the EDX spectrum palladium was detectable with high intensity (Fig. 2d). Peaks featuring zeolite were also found in the spectrum.

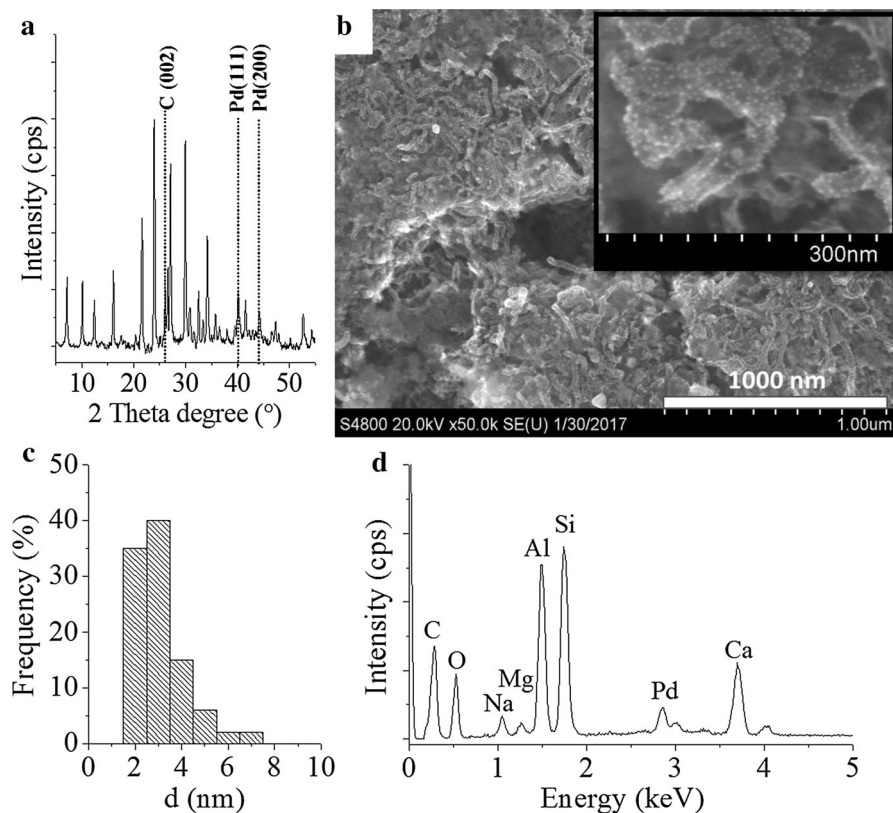


Fig. 2 XRD (X-ray diffraction) pattern (a), SEM (scanning electron microscope) image (b), Pd particle size distribution (c) and EDX (energy-dispersive X-ray spectroscopy) spectra (d) of the Pd/N-CNTs-Zeolite catalyst

Catalytic tests of the Pd/N-CNT-zeolite nanocomposite

Five bar pressure was not enough to achieve the full conversion of nitrobenzene to aniline. Therefore, the pressure was increased and the catalyst was tested at 10 and 20 bar. Based on the results of the hydrogenation tests of the catalyst, the catalyst was active at 10 and 20 bar pressure. After 240 min of hydrogenation, the nitrobenzene conversion was 99.9% at 323 K (Fig. 3). There is no difference between the results of the experiments performed at 10 bar or 20 bar, thus the usage of higher pressure than 10 bar is not necessary. The quantity of the formed aniline was less than the theoretical amount, which can be attributed to the adsorption effect of the carbon nanotubes [22]. The pores of the zeolite core are blocked with amorphous carbon, which was formed during the CCVD process. Therefore, the zeolite is not taking part in the aniline adsorption.

The initial formation rate of aniline (between 5 and 80 min) was increased at 10 bar hydrogen pressure, compared to the case at 5 bar (Fig. 4). After 2 h, the

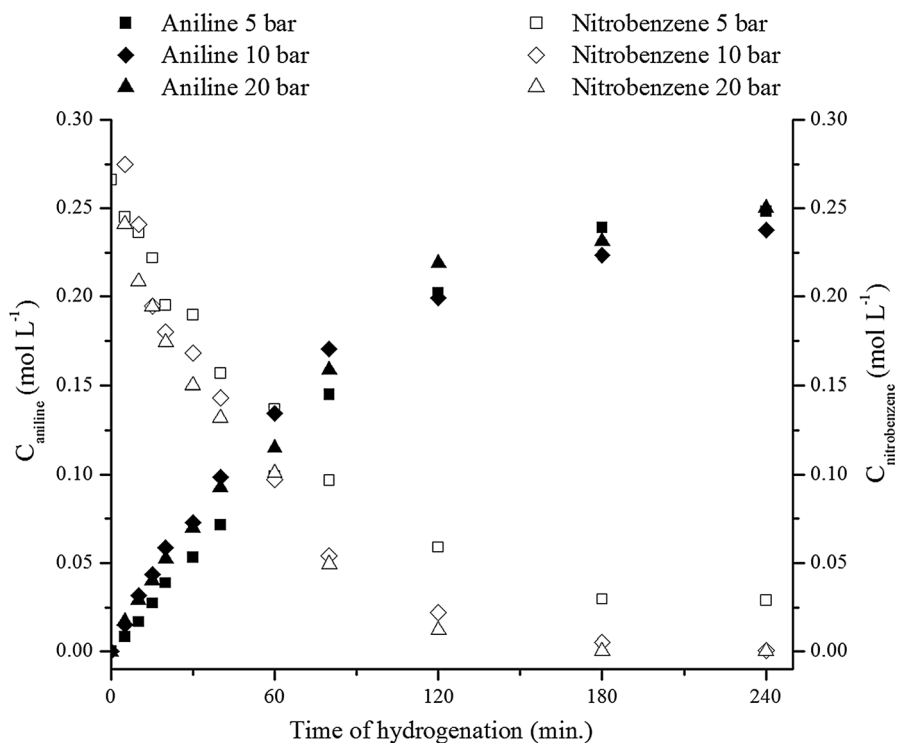


Fig. 3 Nitrobenzene conversion to aniline at 5, 10 and 20 bar and 323 K. 2 g 2 wt% Pd/N-CNT-zeolite nanocomposite catalyst was used

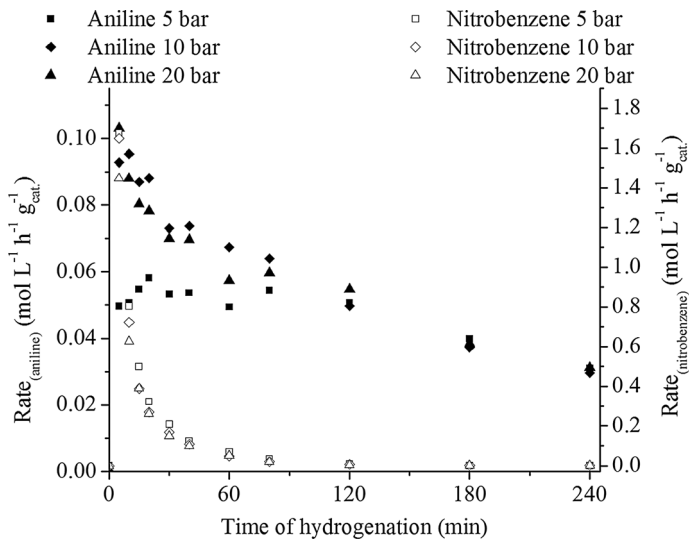


Fig. 4 Reaction rate of aniline formation and nitrobenzene transformation depending on the hydrogenation time

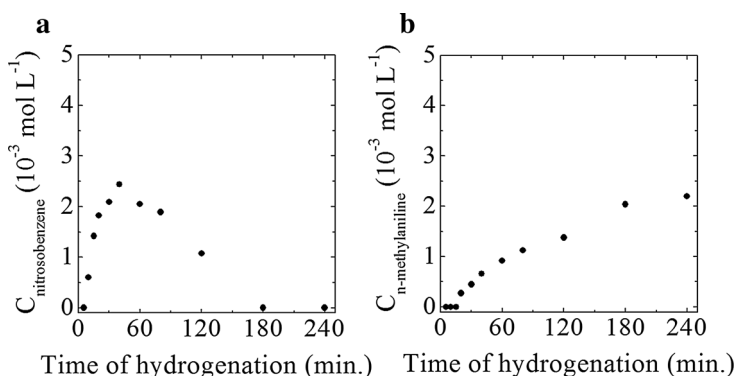


Fig. 5 Formation of nitrosobenzene (a) and *N*-methylaniline (b) during the reaction, at 5 bar and 323 K. 2 wt% Pd/N-CNT-zeolite nanocomposite catalyst was applied

reaction rate has become almost the same. There is no difference between the reaction rate, in case of 10 and 20 bar experiments.

Two by-products were formed during the hydrogenation, each of them in negligible quantities (less than $4 \times 10^{-3} \text{ mol L}^{-1}$), nitrosobenzene and *N*-methylaniline (Fig. 5). The concentration of nitrosobenzene continuously decreased, and completely transformed to aniline after 2 h at 10 and 20 bar pressure, while at 5 bar 3 h is needed (SI, Fig. S2). The concentration of *N*-methylaniline continuously increased depending on the time of hydrogenation, but it was produced in a smaller amount at higher pressure (SI, Fig. S2). In our experiments, other potential intermediates or condensed molecules (e.g. *N*-phenylhydroxylamine, azobenzene or azoxybenzene) did not form, unlike in the case of previous studies [23, 24].

The formation rate of the by-products was higher at 10 and 20 bar, than at 5 bar (SI, Fig. S3). The formation rate of nitrosobenzene was the highest after 15 min at 20 bar and then it was continuously transformed to aniline. The concentration of the *N*-methylaniline was increased continuously in case of all experiments (SI, Fig. S2) and the highest rate of formation was observed after 10–15 min of hydrogenation (SI, Fig. S3). By increasing the hydrogenation pressure, the formation of the *N*-methylaniline can be slightly decreased.

Conclusion

Palladium nanocomposite for catalytic purposes was synthesized based on zeolite supported nitrogen-doped carbon nanotubes. In our work zeolite beads were coated with N-CNT by using the CCVD method. In the prepared samples, the surface of the beads was densely covered by N-CNT. This N-CNT-zeolite system was applied as catalyst support material decorated by palladium nanoparticles. The Pd particles were settled on the surface of the nanotubes and the particle size distribution was relatively homogenous ($< 7 \text{ nm}$). The final Pd/N-CNT-zeolite nanocomposite catalyst was tested in hydrogenation (nitrobenzene/aniline conversion) at different pressures (5, 10 and 20 bar) at 323 K. The activity of the nanocomposite was the

highest at 10 bar. However, there is no significant difference in respect of the catalytic activity, based on the results of the 10 bar and 20 bar experiments. Therefore, it is not necessary to increase the pressure above 10 bar during the studied reaction. Based on the results of the catalytic tests, it can be confirmed that this complex nanocomposite catalysts are efficient materials in hydrogenation of nitro-(NO₂) groups. By applying them, the formation of condensed derivatives and potential by-products (e.g. azobenzene or azoxybenzene), which was detected in previous studies, was avoided. The system was easy to treat and remove from the reaction medium which is another advantage of the zeolite support of the nanotube-based catalysts. Carbon nanotubes are easily form stable dispersion with the reaction medium (thermodynamically stable colloid) which can be avoided by applying the zeolite support and the above described catalyst preparation process.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. TDI/MDI (1999, San Francisco) Process Evaluation/Research Planning Program, Chem Systems Report 98/99 S8
2. Salzinger M, Lercher JA (2011) Reaction network and mechanism of the synthesis of methylenedianiline over dealuminated Y-type zeolites. *Green Chem* 13:149
3. Hatziantoniou V, Andersson B, Schön NH (1986) Mass transfer and selectivity in liquid-phase hydrogenation of nitro compounds in monolithic catalyst reactor with segmented gas–liquid flow. *Ind Eng Chem Proc Des Dev* 25:964–970
4. Holler V, Wegracht D, Yuranov I, Kiwi-Minsker L, Renken A (2000) Three-phase nitrobenzene hydrogenation over supported glass fiber catalysts: reaction kinetics study. *Chem Eng Technol* 23:251–255
5. Burge HD, Collins DJ, Davis BH (1980) Intermediates in the Raney nickel catalyzed hydrogenation of nitrobenzene to aniline. *Ind Eng Chem Prod Res Dev* 19:389–391
6. Collins DJ, Smith AD, Davis BH (1982) Hydrogenation of nitrobenzene over a nickel boride catalyst. *Ind Eng Chem Prod Res Dev* 21:279–281
7. Wisniak J, Klein M (1984) Reduction of nitrobenzene to aniline. *Ind Eng Chem Prod Res De* 23:44–50
8. Zhu J, Holmen A, Chen D (2013) Carbon nanomaterials in catalysis: proton affinity, chemical and electronic properties, and their catalytic consequences. *ChemCatChem* 5:378–401
9. Liao HG, Xiao YJ, Zhang HK, Liu PL, You KY, Hean C, Luo W (2012) Hydrogenation of nitro-cyclohexane to cyclohexanone oxime over Pd/CNT catalyst under mild conditions. *Catal Comm* 19:80–84
10. Fernando M, Pereira JR, Figueiredo L, Serp P, Kalck P, Kihn Y (2004) Catalytic activity of carbon nanotubes in the oxidative dehydrogenation of ethylbenzene. *Carbon* 42:2807–2813
11. Xianlong D, Yongmei L, Jianqiang W, Yong CJ (2013) Catalytic conversion of biomass-derived levulinic acid into γ -valerolactone using iridium nanoparticles supported on carbon nanotubes. *Catal* 34:993–1001

12. Li L, Wu G, Xu BQ (2006) Electro-catalytic oxidation of CO on Pt catalyst supported on carbon nanotubes pretreated with oxidative acids. *Carbon* 44:2973–2983
13. Liang D, Gao J, Sun H, Chen P, Hou Z, Zheng X (2011) Selective oxidation of glycerol with oxygen in a base-free aqueous solution over MWNTs supported Pt catalysts. *Appl Catal B* 106:423–432
14. Li CH, Yu ZX, Yao KF, Ji SF, Liang J (2005) Nitrobenzene hydrogenation with carbon nanotube-supported platinum catalyst under mild conditions. *J Mol Catal A Chem* 226:101–105
15. Liu S, Hao F, Liu P, Luo H (2015) The influences of preparation methods on the structure and catalytic performance of single-wall carbon nanotubes supported palladium catalysts in nitrobenzene hydrogenation. *RSC Adv* 5:22863–22868
16. Guoa X, Donga H, Li B, Donga L, Mua X, Chen X (2017) Influence of the functional groups of multiwalled carbon nanotubes on performance of Ru catalysts in sorbitol hydrogenolysis to glycols. *J Mol Catal A Chem* 426:79–87
17. Ratso S, Kruusenberg I, Joost U, Saar R, Tammeveski K (2016) Enhanced oxygen reduction reaction activity of nitrogen-doped graphene/multi-walled carbon nanotube catalysts in alkaline media. *International journal of hydrogen energy*. *Int J Hydrogen Energy* 41:22510–22519
18. Ibrahim EMM, Khavrus VO, Leonhardt A, Hampel S, Oswald S, Rummeli MH, Büchner B (2010) Synthesis, characterization, and electrical properties of nitrogen-doped single-walled carbon nanotubes with different nitrogen content. *Diamond Relat Mater* 19:1199–1206
19. García-García FR, Álvarez-Rodríguez J, Rodríguez-Ramos I, Guerrero-Ruiz A (2010) The use of carbon nanotubes with and without nitrogen doping as support for ruthenium catalysts in the ammonia decomposition reaction. *Carbon* 48:267–276
20. An W, Turner CHJ (2009) Chemisorption of transition-metal atoms on boron- and nitrogen-doped carbon nanotubes: energetics and geometric and electronic structures. *J Phys Chem C* 113:7069–7078
21. Vanyorek L, Halasi Gy, Pekker P, Kristály F, Kónya Z (2016) Characterization and catalytic activity of different carbon supported Pd nanocomposites. *Catal Lett* 146:2268–2277
22. Al-Johani H, A-Salam M (2011) Kinetics and thermodynamic study of aniline adsorption by multi-walled carbon nanotubes from aqueous solution. *J Coll Int Sci* 360:760–767
23. Turáková M, Salmi T, Eranen K, Worná J, Y-Murzin D (2015) Liquid phase hydrogenation of nitrobenzene. *Appl Catal A Gen* 499:66–76
24. Dong B, Li Y, Ning X, Wang H, Yu H, Peng F (2017) Trace iron impurities deactivate palladium supported on nitrogen-doped carbon nanotubes for nitrobenzene hydrogenation. *Appl Catal A Gen* 545:54–63

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