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Short Communication

Hydrogenation of nitrocyclohexane to cyclohexanone oxime over Pd/CNT catalyst under mild conditions

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1. Introduction

ε-Caprolactam is an important petrochemical primarily used to synthesize nylon-6 fibers and resins. The current commercial production of ϵ -caprolactam is mainly based on the traditional route, cyclohexane is oxidized to cyclohexanone, and then cyclohexanone can be further converted to cyclohexanone oxime and lactam via ammoximation and Beckmann Rearrangement [1]. The processes for the production of cyclohexanone oxime mainly include cyclohexanone-hydroxylamine and ammoximation of cyclohexanone [2-4]. It should be noted that cyclohexanone is obtained from cyclohexane oxidation, which is a very low efficient process with per pass vield of 4-5% without catalyst and 8-10% catalyzed by cobalt catalyst [5.6]. Moreover, the processes for the production of cyclohexanone oxime involve multi-step reactions and result in the formation of a large amount of ammonium sulfate and wastes. To overcome the above-mentioned problems, there have been many attempts to find novel and environmental friendly methods for the production of cyclohexanone oxime. One step hydrogenation of nitrocyclohexane to cyclohexanone oxime is an alternative method. However, previous studies show that the process catalyzed by a supported Pd catalyst in the presence of PbO salts or salts of Cu (II) and Ag (I) homogeneous catalyst has drawbacks such as high pressure and the formation of environmental unfriendly inorganic wastes [7-9]. Recent progresses in the nitration of cyclohexane to nitrocyclohexane with high selectivity urge the research interest on one step hydrogenation of nitrocyclohexane to cyclohexanone oxime [10,11]. Serna et al. [12]

ABSTRACT

The Pd/C, Pt/C, Ni/CNT and Pd/CNT catalysts were prepared by impregnation method and characterized by BET, XRD, TEM and H₂ chemisorption. These catalysts were tested in the hydrogenation of nitrocyclohexane to cyclohexanone oxime. The results show that 5% Pd/CNT catalyst exhibits good performance, it gives nitrocyclohexane conversion of 97.6% and cyclohexanone oxime selectivity of 85.9% under mild conditions of 0.2 MPa and 323 K. The products include cyclohexanone oxime, cyclohexylamine, cyclohexanol and N-cyclohexylamine. It has been found that higher temperature is in favor of the formation of cyclohexylamine, while the amount of cyclohexanol decreases with the increment of reaction temperature.

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have prepared a decorated Pt/TiO₂ catalyst doped with sodium cation, which could reduce nitrocyclohexane to cyclohexanone oxime with a selectivity of 84.5% at 95% conversion under 4.0 MPa and 383 K. Shimizu et al. [13] have developed a heterogeneous Au/Al₂O₃ catalyst on selective hydrogenation of nitrocyclohexane, which exhibits high cyclohexanone oxime yield under 0.6 MPa and 373 K.

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have received increasing attention since they were discovered in 1991 [14]. The outstanding properties of CNTs and CNFs make them become one of the most promising catalyst support materials for heterogeneous catalytic reactions, especially for liquid-phase reactions [15–17]. The first study that CNTs and CNFs were used as catalyst supports started from 1994 [18]. CNTs and CNFs supported components such as Pd, Pt, Ru, Rh, Fe or Ni are mainly used in catalytic hydrogenation processes [16-28]. Geus et al. have reported that CNTs and CNFs materials undergone suitable treatment can be good candidates as the supports for Pd in liquid phase medium [20]. However, there are no reports on the study of partial hydrogenation of nitrocyclohexane to cyclohexanone oxime catalyzed by Pd/CNTs. In this paper, Pd/ CNTs were prepared and characterized, and their catalytic properties in nitrocyclohexane hydrogenation under mild conditions of lower temperature and pressure are performed.

2. Experimental

2.1. Materials

Nitrocyclohexane (97 wt.%) was purchased from Tokyo Chemical Industry Corporation Limited. CNTs were purchased from Shenzhen Nanotech Port Corporation Limited and active carbon was purchased

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from Baoji Rock New Materials Corporation Limited. PdCl₂ and ethylenediamine were analytical grade and purchased from Sinopharm Chemical Reagent Corporation Limited. H₂ (99.99%) was provided by Zhuzhou Diamond Gas Company.

2.2. Catalyst preparation

The CNTs and active carbon were pretreated in concentrated nitric acid (68 wt.%) overnight, recovered by vacuum filtration, washed with distilled water, and dried in vacuum at 383 K for 12 h.

Pd/CNT catalyst was prepared by incipient impregnation method. PdCl₂ was used as the precursor of the active component. 0.2 g PdCl₂ was dissolved into a solution of 1.2 g concentrated hydrochloric acid (38 wt.%) and 10 g distilled water under ultrasonication for 30 min. Then the sodium hydroxide solution (10 wt.%) was dropped into the above solution to regulate pH to 5. Afterwards, the pretreated CNTs were impregnated in the above prepared H₂PdCl₄ solution for 10 h at 303 K under stirring. Finally, the mixture was dried at 383 K for 12 h under vacuum and then was calcinated at 473 K for 4 h under 40 mL/min of nitrogen flow and reduced at 523 K for 3 h under 40 mL/min of hydrogen. Pd/C catalyst was prepared by the similar method except that the support was replaced by active carbon. Pt/C catalyst was prepared by using H₂PtCl₆ \cdot 6H₂O as precursor and Ni/CNT catalyst was prepared by using nickel acetate as precursor.

2.3. Catalyst characterization

Specific surface area, pore volume and pore size distribution of the samples were obtained from the nitrogen adsorption–desorption on a Quantachrome NOVA-2200e automated gas sorption system.

Powder X-ray diffraction (XRD) patterns were determined under an Aolong Y-2000 diffractometer using Cu K α radiation ($\lambda = 1.542$ Å). The tube voltage was 40 kV, the current was 30 mA, and the scan range was $2\theta = 5-90^{\circ}$ with a scanning rate of 1° min⁻¹.

The microstructure of the Pd/CNTs was observed by transmission electron microscopy (TEM) on a Tecnai G² 20 ST electron microscope working under 200 kV. The instrumental magnification ranged from 2×10^4 to 10×10^6 . The samples were deposited on a copper grid and coated with a holey carbon film.

Hydrogen chemisorption was measured on a TP-5080 automated sorption system. The samples had been previously reduced under the same conditions of the catalyst preparation and the hydrogen chemisorption was performed at 323 K.

2.4. Procedures for the catalytic test

Nitrocyclohexane hydrogenation was carried out in a 50 mL Teflon-lined stainless-steel autoclave equipped with temperature detector and pressure control. Typically, 1.29 g nitrocyclohexane (97 wt.%), 10 mL ethylenediamine solvent and 0.2 g catalyst were added into the autoclave. The reactor was sealed, purged with H₂ to replace the air, and then it was heated to the required temperature and pressurized to 0.2 MPa with H₂ under stirring. The catalysts were removed from the solution by filtration when the reaction was finished. The products were identified by GC–MS (SHIMADZU, QP2010 PLUS) and by comparison with commercially pure products. The contents of the raw material and the products were determined by GC (GC-14C, SHIMADZU) with a flame ionization detector (FID) and a 30 m DB-1701 capillary column using naphthalene as an internal standard.



Fig. 1. N_2 adsorption–desorption isotherms and BJH pore size distributions (inset) of 5% Pd/C and 5% Pd/CNTs.

3. Results and discussions

3.1. Characterization of catalysts

Fig. 1 shows the nitrogen adsorption-desorption curves of 5% Pd/ CNTs and 5% Pd/C. Pd/C exhibits a much higher nitrogen adsorption capacity than Pd/CNTs. The isotherm of Pd/C shows an adsorption isotherm of type I according to the IUPAC classification, representing capillary condensation of nitrogen within the uniform microporous structure. Pd/CNTs show an adsorption isotherm of type III, which indicates weak interaction between Pd/CNTs and nitrogen. The hysteresis loop of Pd/C is of type H4 which is associated with slit-shaped pores and Pd/CNTs are of type H1 which is attributed to cylindrical pores with both sides open. According to the geometrical effect and Kelvin equation, bigger area of the hysteresis loop indicates more pores, which is in good agreement with the pore volume in Table 1. Higher relative pressure at the closure point of the hysteresis loops indicates bigger pore diameter, which is also consistent with the pore diameter distribution in Fig. 1. A broad pore size distribution is observed in Pd/CNTs, and its average pore size calculated from the desorption branch by the BJH model is 17.8 nm. However, Pd/C shows a narrow pore size distribution with the average pore size of 1.7 nm. It can be seen from Table 1 that the BET surface area of Pd/C $(907 \text{ m}^2 \text{ g}^{-1})$ is much larger than Pd/CNTs $(72 \text{ m}^2 \text{ g}^{-1})$. The TEM images of Pd/CNTs and Pd/C are shown in Fig. 2. The TEM micrographs of Pd/CNTs and Pd/C show that palladium particles are well dispersed on the surface of the supports. Statistical results demonstrate that palladium particle size in Pd/C ranges from 2.9 to 5.1 nm, and palladium particle in Pd/CNTs is slightly smaller than that in Pd/C ranging from 2.2 to 4.4 nm. Fig. 3 presents the XRD patterns of Pd/CNTs and Pd/C. Both of the samples exhibit significant feature diffraction peak around $2\theta = 25^{\circ}$ corresponding to (002) crystalline plane of charcoal.

Table 1		
Textural	properties of different catalysts.	

Catalysts	BET surface areas $(m^2 g^{-1})$	Pore diameter (nm)	Pore volume (cm ³ g ⁻¹)
5% Pd/C	907	1.7	0.41
5% Pt/C	1058	1.4	0.63
20% Ni/CNTs	65	18.0	0.29
5% Pd/CNTs	72	17.8	0.31



Fig. 2. TEM images of 5% Pd/C (a, b) and 5% Pd/CNTs (c, d).

There are very weak peaks of Pd presenting on the pattern of Pd/ CNTs, which indicates that the Pd particles are well dispersed on CNTs. In the XRD pattern of Pd/CNTs, there are seven strong and spiculate peaks which are attributed to sodium chloride formed during the procedure of catalyst preparation. XRD peaks of Pd in the Pd/CNTs are broader than those in Pd/C, which further confirms the fact of smaller average particle size of Pd on CNT support. Table 2 shows the hydrogen chemisorption measurements of 5% Pd/C and 5% Pd/CNTs. The results also indicate that the dispersion of palladium particles on CNTs is higher than that on carbon, which are in accord with the results of XRD patterns and TEM images.



Fig. 3. XRD patterns of 5% Pd/C and 5% Pd/CNTs.

3.2. Catalytic performance

The prepared catalysts were tested in liquid phase hydrogenation of nitrocyclohexane to cyclohexanone oxime under mild conditions of 0.2 MPa and 323 K in a Teflon-lined stainless-steel autoclave using ethylenediamine as solvent. The effects of H₂ pressure and agitation rate were investigated and the results show that the selectivity of cyclohexanone oxime increases with the increments of H₂ pressure from atmosphere pressure to 0.2 MPa and agitation rate from 500 rpm to 1100 rpm. However, the cyclohexanone oxime selectivity has no significant change with the further increments of pressure and agitation rate. Therefore, the hydrogenation of nitrocyclohexane was tested under the conditions of 0.2 MPa and 1100 rpm.

Nitro compound hydrogenation on metal catalysts depends not only on the nature of metal, but also on the crystallite size and the reactant interacts with the support [29-31]. It was reported that Pt/Al₂O₃, Pt/C or Pd/C was able to catalyze nitrocyclohexane hydrogenation to cyclohexanone oxime using ethanol as solvent. However, it is of very low selectivity to cyclohexanone oxime (less than 25%) and the corresponding amine is the main product through the complete reduction of the nitro group [12]. It has been reported that Pt nanoparticles decorated with TiOx and modified with sodium cations improved cyclohexanone oxime selectivity to 84.5% at 95% conversion under 4.0 MPa and 383 K using ethanol as solvent [12]. Au/Al₂O₃ with smaller Au particle size (2.5 nm) exhibited high cyclohexanone oxime yield under 0.6 MPa and 373 K also using ethanol as solvent [13]. We test this reaction with Ni, Pd, Pt supported catalysts using ethylenediamine as solvent under mild conditions of 0.2 MPa and 323 K. As shown in Table 3, besides cyclohexanone oxime, the main by-products include cyclohexylamine, cyclohexanol and Ncyclohexylhydroxylamine. The N-cyclohexylhydroxylamine is testified to be an intermediate, which mainly can be further hydrogenated to cyclohexylamine. Ni/CNT catalyst is able to catalyze nitrocyclohexane

Table 2	
Hydrogen chemisorption datas of 5% Pd/C and 5% Pd/CNTs.	

Catalysts	H ₂ uptake (µmol g ⁻¹)	Metallic surface areas $(m^2 g^{-1})$	Dispersion (%)
5% Pd/C	16.3	39.4	6.9
5% Pd/CNTs	22.1	53.5	9.4

Table 3	
The results of nitrocyclohexane hydrogenation over different catalysts.	

Catalyst	Time (h)	%Conversion (NCH)	%Selectivity			
			CHO	CHA	CHOL	CHOA
5% Pd/C	3	100	55.1	6.2	7.9	30.8
5% Pt/C	1	76.3	36.4	6.1	10.5	47.0
20% Ni/CNTs	6	62.9	21.6	28.9	22.8	26.7
5% Pd/CNTs	6	97.6	85.9	5.0	2.9	6.2

NCH-nitrocyclohexane; CHO-cyclohexanone oxime; CHA-cyclohexylamine; CHOL-cyclohexanol; CHOA-N-cyclohexylhydroxylamine.

Reaction conditions: T = 323 K, $P_{H2} = 0.2$ MPa.

to cyclohexanone oxime with lower selectivity, but more cyclohexylamine and cyclohexanol are obtained. The nitrocyclohexane conversion achieves to 76.3% with cyclohexanone oxime selectivity of 36.4% catalyzed by Pt/C for 1 h. The catalytic performance of Pd/C is better than Pt/C, the nitrocyclohexane is completely converted after 3 h and the selectivity to cyclohexanone oxime increases to 55.1%. Pd/CNT catalyst gives the best result of nitrocyclohexane conversion of 97.6% and cyclohexanone oxime selectivity of 85.9%, along with a small amount of cyclohexylamine and cyclohexanol. The reason may be that smaller Pd particle size and higher Pd surface area on CNTs present higher activity and local higher hydrogen concentration caused by higher H₂ adsorption capacity in Pd/CNTs is of benefit to the formation of cyclohexanone oxime. In our work, ethylenediamine was tested to be a more suitable solvent than ethanol, acetonitrile and cyclohexylamine under the catalvsis of Pd/CNTs and Pd/C, which is different from the report of P. Serna et al. [12] and K.-i. Shimizu et al. [13] using ethanol as solvent under the catalysis of Pt/TiO₂ and Au/Al₂O₃. The results show that the cyclohexanone is not detected according to the GC-MS and the comparison with commercially pure product. Therefore, cyclohexyl-cyclohexylidene amine and 2-cyclohexylidene cyclohexanone generated from cyclohexanone do not emerge. Since Pd/CNT catalyst gives better results for nitrocyclohexane hydrogenation to cyclohexanone oxime, we focus on



Fig. 4. The effect of reaction time on nitrocyclohexane hydrogenation over 5% Pd/CNTs. Reaction conditions: stirring rate, 1100 rpm; $P_{H2} = 0.2$ MPa; T = 323 K.



Fig. 5. The effect of reaction temperature on nitrocyclohexane hydrogenation over 5% Pd/CNTs. Reaction conditions: stirring rate, 1100 rpm; $P_{H2} = 0.2$ MPa; t = 6 h.

the influence of Pd loading amount as well as reaction time and reaction temperature. Results in Fig. 4 show that 5% Pd/CNTs give nitrocyclohexane conversion of 100% and cyclohexanone oxime selectivity of 71% at 7.5 h under 0.2 MPa and 323 K. It gives the best result of nitrocyclohexane conversion of 97.6% and cyclohexanone oxime selectivity of 85.9% at 6 h. The results show that the catalytic activity decreases with the decrement of the Pd loading amount. The nitrocyclohexane conversion is only 47.2% under the catalysis of 3% Pd/CNTs for 8 h, and it reaches to 99.4% till 24 h with the cyclohexanone oxime selectivity of 82.8%.

The effects of reaction time and reaction temperature over 5% Pd/CNTs were discussed. Nitrocyclohexane hydrogenation over 5% Pd/CNTs at different reaction time was carried out at 323 K. As shown in Fig. 4, as the reaction time proceeds from 1 h to 2 h, the conversion of nitrocyclohexane increases greatly from 47.2% to 82.9%, and the nitrocyclohexane is completely converted at 7.5 h. The selectivity to cyclohexanone oxime increases gradually from 71.0% to 85.9% and then declines to 71.8% with the extending of the reaction time. It is confirmed that the performance of catalyst is related to the size and the surface area of the active metal nanoparticles and its support, which could regulate the adsorption and activation of substrates and desorption of products by controlling the number of corner, edge and face atoms of the catalysts [32-34]. Compared with Pd/C and Pt/C catalyst, the smaller Pd particle size, higher Pd surface area and CNTs support are helpful to the production of cyclohexanone oxime.

The effect of reaction temperature on the nitrocyclohexane hydrogenation over 5% Pd/CNTs was investigated in the temperature range from 313 K to 353 K for 6 h. It can be seen from Fig. 5 that the nitrocyclohexane conversion increases with the increment of reaction temperature under the same reaction time and pressure, however, the selectivity to cyclohexanone oxime achieves to the maximum value of 85.9% at 323 K and then decreases with the increment of reaction temperature. Results in Fig. 5 show that higher temperature is in favor of the formation of cyclohexylamine, while the amount of cyclohexanol decreases with the increment of reaction temperature.

4. Conclusions

The Pd/C, Pt/C, Ni/CNT and Pd/CNT catalysts were prepared by impregnation method and characterized by BET, XRD, TEM and H_2 chemisorption. 5% Pd/CNT catalyst exhibits good performance on nitrocyclohexane hydrogenation to cyclohexanone oxime, it gives nitrocyclohexane conversion of 97.6% and cyclohexanone oxime

selectivity of 85.9% under mild conditions of 0.2 MPa and 323 K. The effects of Pd loading amount, reaction time and reaction temperature are discussed, higher temperature is in favor of the formation of cyclohexylamine and the amount of cyclohexanol decreases with the increment of reaction temperature.

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