Catalysis Communications 50 (2014) 9–12

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Nitrocyclohexane hydrogenation to cyclohexanone oxime over mesoporous carbon supported Pd catalyst

Yanhua Yan, Sihua Liu, Fang Hao, Pingle Liu *, He'an Luo

College of Chemical Engineering, Xiangtan University, Xiangtan 411105, China

ARTICLE INFO

Article history:
Received 23 January 2014
Received in revised form 19 February 2014
Accepted 21 February 2014
Available online 28 February 2014

Keywords:
Nitrocyclohexane
Hydrogenation
Mesoporous carbon
Palladium supported catalyst
Cyclohexanone oxime

ABSTRACT

Mesoporous carbon materials (MC) were prepared by soft template, hard template and hydrothermal synthesis methods. And mesoporous carbon supported palladium catalysts were obtained from incipient impregnation method. The prepared samples were characterized by nitrogen adsorption–desorption, X-ray diffraction, transmission electron microscopy and hydrogen chemisorption. Palladium supported on mesoporous carbon prepared by hard template method shows better catalytic performance, it gives the 82.2% selectivity to cyclohexanone oxime at the nitrocyclohexane conversion of 99.4% under the mild reaction conditions of 0.5 MPa and 323 K.

1. Introduction

Oximes are highly valuable organic intermediates because of their wide application for polymer, perfumes and paint, and particularly more attention has been given to the synthesis of cyclohexanone oxime in view of its usage as the precursor for the production of ε-caprolactam and Nylon-6. The current commercial production method for cyclohexanone oxime is mainly based on the traditional route that cyclohexane is oxidized to cyclohexanone through a very low efficient process with per pass yield of 4–5% without catalyst or 8–10% catalyzed by cobalt catalyst [1,2], and then cyclohexanone oxime is obtained by cyclohexanone–hydroxylamine or ammoximation of cyclohexanone [3,4]. However, the above route is less desirable for large scale production owing to its low atom economy, complex technology, serious environmental problems and equipment corrosion [5]. To overcome the above-mentioned disadvantages, there have been many attempts to find novel and environmentally friendly methods for the production of cyclohexanone oxime [6,7]. The ammoximation of cyclohexanone to cyclohexanone oxime over TS-1 in an isopropanol-based solvent system with high yield has improved atom economy greatly. However, process optimization, reactor design and catalyst improvement have been restricted due to non-depth research of the reaction mechanism and kinetics behavior [8,9]. Nitrocyclohexane hydrogenation process developed by DuPont is an alternative promising method [10,11], especially cyclohexane nitration process has made significant progress [12,13]. Serna et al. [14] have prepared a sodium decorated Pt/TiO$_x$ catalyst, which could reduce nitrocyclohexane to cyclohexanone oxime with the selectivity of 84.5% at 95.0% conversion under 4.0 MPa and 383 K. Shimizu et al. [15] have developed a heterogeneous Au/Al$_2$O$_3$ catalyst, and the catalyst with smaller size gold particles gives a high cyclohexanone oxime yield under 0.6 MPa and 373 K. Liu et al. [16] have found that single walled carbon nanotube (SWCNT) supported Pd is effective for the reaction and it gives 97.7% conversion of nitrocyclohexane and 97.4% selectivity toward cyclohexanone oxime for its mesoporous structure with pore size range from 2 to 50 nm, while activated carbon (AC) with microporous structure supported palladium only gives a cyclohexanone oxime yield of 64.1%. However, carbon nanotube especially SWCNT is extremely difficult to prepare on large scale and is quite expensive.

Mesoporous carbon has attracted rapidly growing attention and has been intensively studied for its remarkable functional properties, which make it one of the most promising catalyst support materials for heterogeneous catalytic reaction. The methods including catalytic gasification, carbon aerogel through sol–gel process and template method have been proposed to introduce mesopores in activated carbon [17–19].

In this paper, mesoporous activated carbon was prepared and used as support to obtain Pd/MC catalyst, and it presents better catalytic performances in nitrocyclohexane hydrogenation to cyclohexanone oxime than microporous activated carbon.

---

* Corresponding author. Tel.: +86 731 58298005; fax: +86 731 58298172.
E-mail address: liupingle@xtu.edu.cn (P. Liu).

http://dx.doi.org/10.1016/j.catcom.2014.02.020
1566-7367/© 2014 Elsevier B.V. All rights reserved.

2. Experimental

2.1. Materials

Nitrocyclohexane (95 wt.%) was purchased from Tokyo Chemical Industry Corporation Limited. Commercial activated coal carbon (ACC) was purchased from Baoji Rock New Materials Corporation Limited. $PdCl_2$ and ethylenediamine were analytical grade and purchased from Sinopharm Chemical Reagent Corporation Limited. H_2 (99.9%) was provided by Zhuzhou Diamond Gas Company.

2.2. Catalyst preparation

Mesoporous carbons prepared by soft template method [20] from different raw materials are labeled as SMC-1 and SMC-2, mesoporous carbons prepared by hard template method are marked as HMC-1 and HMC-2 [21], and the sample prepared by triblock copolymer and phenolic resin precursor via hydrothermal synthesis method is signed as HTMC [22].

The catalysts are prepared as the following steps. MC and ACC were pretreated in concentrated nitric acid (68 wt.%) overnight, and the sample was filtrated and washed by distilled water, and then dried in vacuum at 383 K for 10 h. Pd/MC catalyst was prepared by incipient impregnation method. 0.14 g $PdCl_2$ was dissolved into a solution of 1.1 g concentrated hydrochloric acid (38 wt.%) and 10 g ultrapure water under ultrasonication for 5 min. Then the sodium hydroxide solution (10 wt.%) was dropped into the above solution to adjust the pH to 5–6. Afterwards, the pretreated support was impregnated into the above prepared H_2PdCl_4 solution for 10 h at 298 K under magnetic stirring, and then the mixture was dried at 383 K for 10 h under vacuum. Finally, the sample 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.

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 Kα radiation ($\lambda = 1.542$ Å). The tube voltage was 40 kV, the current was 30 mA, and the scan range was $2\theta = 5$–$90°$ with a scanning rate of $1° min^{-1}$. The microstructure of the catalysts was observed by transmission electron microscopy (TEM) on a Tecnai $G^2$20 ST electron microscope working under 200 kV. The instrumental magnification ranged from 2×10^4 to 10×10^6. The sample was deposited on a copper grid and coated with a holey carbon film. Hydrogen chemisorption was measured on a TP-5080 automated sorption system. The sample had been previously reduced under the same conditions as the catalyst preparation and the hydrogen chemisorption was performed at 323 K.

2.4. Typical procedures for the catalytic test

The catalytic process was performed in a 50 mL Teflon-lined stainless-steel autoclave equipped with magnetic stirring. Briefly, 0.56 g nitrocyclohexane (95 wt.%), 5 mL ethylenediamine solvent and 0.1 g catalyst were added into the autoclave. The reactor was sealed and the hydrogen was used for replacing the air, then the autoclave was heated to 323 K and pressurized to the required pressure under continuous stirring. The catalysts were separated from the reaction solution by vacuum filtration when the reaction was completed. The products were identified by GC–MS (SHIMADZU, QP2010 PLUS). The content of the products was determined by GC (GC-14C, SHIMADZU) with a flame ionization detector (FID) using dimethyl phthalate (DMP) as the internal standard.

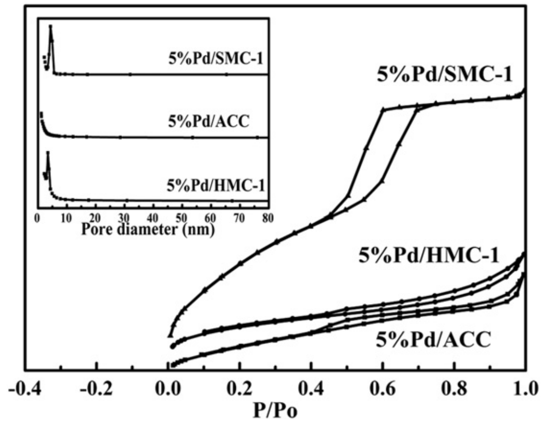

Fig. 1. N_2 adsorption–desorption isotherms and BJH pore size distribution (inset) of 5% Pd/HMC-1, 5% Pd/SMC-1 and 5% Pd/ACC.

3. Results and discussions

3.1. Characterization of catalysts

Fig. 1 shows the nitrogen adsorption–desorption curves of Pd/HMC-1, Pd/SMC-1 and Pd/ACC. The isotherm of Pd/ACC shows an adsorption isotherm of type I according to the IUPAC classification and has a H_4 hysteresis loop, representing capillary condensation of nitrogen within the uniform slit-shaped microporous structure. Pd/HMC-1 shows an adsorption isotherm of type IV with a H_4 hysteresis loop, the volume absorbed for nitrogen increase at relative pressure (p/p_0) of approximately 0.4–0.8, which indicates capillary condensation of nitrogen within the uniform mesoporous structure. Pd/SMC-1 shows a typical type IV isotherm and has a H_1 hysteresis loop, indicating the mesoporous structures of the materials. It's known that bigger area of the hysteresis loop indicates more pores from the geometrical effect and Kelvin equation, which is in good agreement with the pore volume in Table 1 that Pd/SMC-1 has the largest volume. Meanwhile, higher relative pressure at the closure point of the hysteresis loops indicates bigger pore diameter, which is also consistent with the result in Table 1 that the pore sizes of Pd/HMC-1 and Pd/SMC-1 calculated from the desorption branch by the BJH model are respectively 3.4 and 4.4 nm. While Pd/ACC shows a narrow pore size distribution with the average pore size of 1.7 nm. The textural properties of the supports have a great effect on their catalytic performance. The results indicate that mesoporous carbon-supported palladium catalysts with suitable surface area and volume show better catalytic performance.

The TEM images of Pd/ACC, Pd/HMC-1 and Pd/HTMC are shown in Fig. 2. The TEM micrographs of the catalysts show that palladium particles are well dispersed on the surface of the supports. Statistical results indicate that palladium particles in Pd/ACC range from 2.9 to 11.4 nm. Palladium particles in Pd/HTMC range from 4.5 to 11.1 nm, palladium particles in Pd/HMC-1 range from 3.6 to 10.4 nm. We can find that

Table 1
Textural properties of different catalysts.

Catalysts	Surface area (m^2g^{-1})	Average pore size (nm)	Pore volume (cm^3g^{-1})
5% Pd/HMC-1	421.63	3.43	0.42
5% Pd/HMC-2	649.24	3.43	0.70
5% Pd/HTMC	4.30	3.81	0.01
5% Pd/ACC	456.23	1.70	0.31
5% Pd/SMC-1	1186.80	4.35	1.00
5% Pd/SMC-2	455.12	3.84	0.13

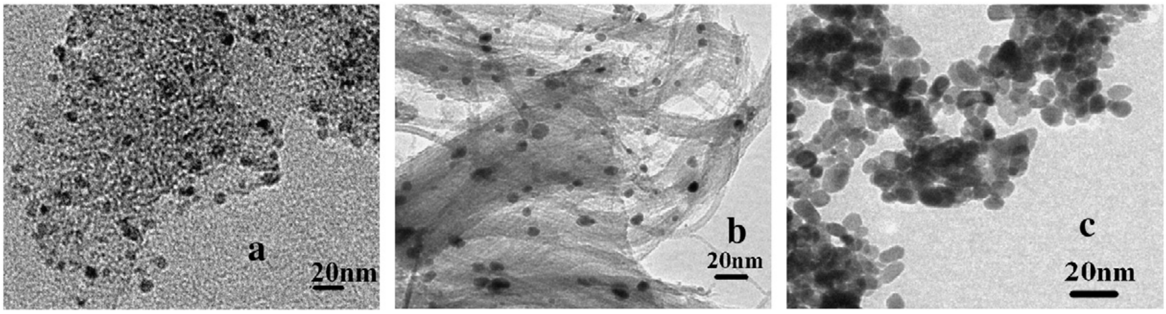

Fig. 2. TEM images of 5% Pd/ACC (a), 5% Pd/HMC-1 (b) and 5% Pd/HTMC (c).

Pd/HMC-1 (Fig. 2 (b)) presents lamellar structure and Pd/HTMC presents nutty structure.

Fig. 3 shows the XRD patterns of the prepared catalysts. The catalysts exhibit characteristic diffraction peaks of carbon's crystalline plane around $2\theta = 26°$, and the peaks at $2\theta = 40$ and $47°$ are ascribed to the characteristic diffraction peak of palladium. Pd/HMC, Pd/HTMC and Pd/ACC exhibit three strong and characteristic peaks at $2\theta = 32$, 45, and 57° which are corresponding to sodium chloride. There are very weak peaks of Pd with different directions around $2\theta = 40°$ and $2\theta = 46°$ respectively in Pd/HMC-1, Pd/HMC-2 and Pd/HTMC which demonstrates that Pd particles are well dispersed on carbon. Moreover, Pd/ACC does not present obvious characteristic diffraction peaks of Pd particles, which also indicates that the Palladium particles are well dispersed on carbon. Table 2 shows the hydrogen chemisorption measurements of Pd/HMC-1, Pd/HMC-2, Pd/HTMC and Pd/ACC. The results demonstrate that the dispersion of palladium particles on mesoporous carbon is better than that on microporous coal carbon.

3.2. Catalytic performance

The results of nitrocyclohexane hydrogenation to cyclohexanone oxime over different catalysts are shown in Table 3. It can be seen from Table 3 that 5% Pd/HMC-1 gives the best result of nitrocyclohexane conversion of 99.1% and cyclohexanone oxime selectivity of 78.8%, and 5% Pd/HTMC presents the highest selectivity to cyclohexanone oxime, however, the catalytic activity is influenced by its very small surface area and pore volume, while the nitrocyclohexane conversion is only 71.4% at the same reaction conditions. The surface area, pore size, pore volume and the metal crystallite size have great effects on the activity and selectivity of the catalyst [23,24]. Mesoporous structure material supported palladium catalysts show higher selectivity to cyclohexanone oxime than microporous coal carbon supported palladium catalyst. The reason may be that the surface channel of the AAC is easier to be blocked. And better dispersion of Pd particle and higher Pd surface area on MC are in favor of producing cyclohexanone oxime. Moreover, too high surface area or too small pore volume is unfavorable for cyclohexanone oxime formation.

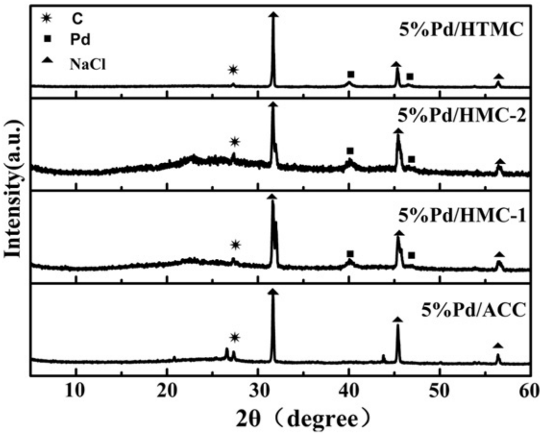

Fig. 3. XRD patterns of 5% Pd/ACC, 5% Pd/HMC-1, 5% Pd/HMC-2 and 5% Pd/HTMC.

Furthermore, the effect of reaction temperature and pressure was discussed. The results are shown in Figs. 4 and 5. Firstly, nitrocyclohexane hydrogenation over 5% Pd/HMC-1 at different reaction temperatures was carried out at 6 h and 0.3 MPa. It can be seen from Fig. 4 that a little higher temperature can promote the selectivity to cyclohexanone oxime, but the selectivity to cyclohexanone oxime starts to decrease if the temperature is higher than 323 K. And Fig. 5 shows that the effect of the pressure on the selectivity to cyclohexanone oxime has the similar tendency as reaction temperature. The suitable pressure is about 0.5 MPa. Under the optimum reaction conditions, 5% Pd/HMC-1 gives 82.2% selectivity to cyclohexanone oxime at the nitrocyclohexane conversion of 99.4%.

4. Conclusion

In this paper, mesoporous carbons were prepared by different methods, and the prepared mesoporous carbons were used as the support to obtain the palladium supported catalyst by incipient impregnation method. Mesoporous structure carbon supported palladium catalysts show better catalytic performance. 5% Pd/HMC-1 gives 82.2% selectivity to cyclohexanone oxime at the nitrocyclohexane conversion of 99.4% under the mild reaction condition of 0.5 MPa and 323 K. It may provide a low cost catalyst for nitrocyclohexane hydrogenation to cyclohexanone oxime.

Table 2

Hydrogen chemisorption data of different catalysts.

Catalysts	H_2 uptake (μmolg^{-1})	Metallic surface areas (m^{2}g^{-1})	Dispersion (%)
5% Pd/HMC-1	10.04	19.04	4.27
5% Pd/HMC-2	16.55	31.40	7.05
5% Pd/HTMC	5.84	0.55	2.49
5% Pd/ACC	4.09	7.75	1.74

Table 3

The results of nitrocyclohexane hydrogenation over different catalysts.

Catalyst	% Conversion (NCH)	% Selectivity		
		CHO	CHA	CHN
5% Pd/HMC-1	99.08	78.81	9.10	1.48
5% Pd/HMC-2	99.72	61.88	1.514	1.96
5% Pd/HTMC	71.41	82.87	1.318	0.25
5% Pd/ACC	99.14	53.74	4.314	0.76
5% Pd/SMC-1	99.77	59.43	1.379	0.56
5% Pd/SMC-2	99.87	58.22	9.878	0.38

NCH—nitrocyclohexane; CHO—cyclohexanone oxime; CHA—cyclohexylamine; CHN—cyclohexanone.

Reaction conditions: T = 323 K, P_{H2} = 0.3 MPa, t = 6 h, n = 1100 pm.

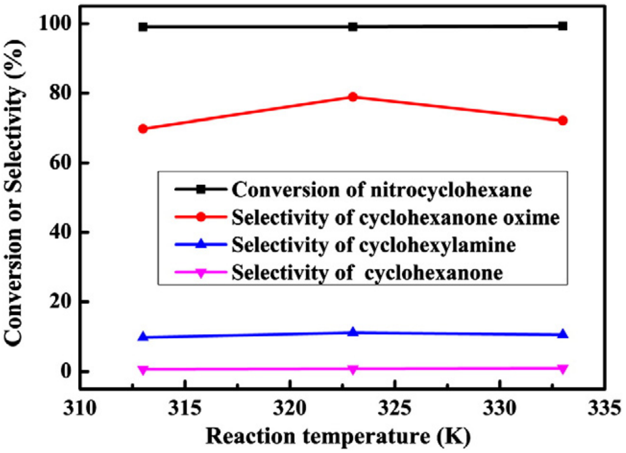

Fig. 4. Effect of reaction temperature on nitrocyclohexane hydrogenation.

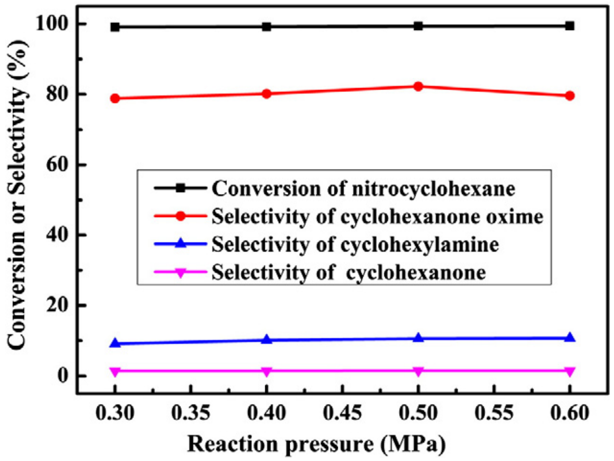

Fig. 5. Effect of reaction pressure on nitrocyclohexane hydrogenation.

Acknowledgments

This work was supported by the NSFC (21276218), Program for New century Excellent Talents in University (NCET-10-0168), SRFDP (2012430110007), Scientific Research Fund of Hunan Provincial Education Department (13k043) and Project of Hunan Provincial Science & Technology Department (2012Fj1001).

References

[1] H.X. Yuan, Q.H. Xia, H.J. Zhan, X.H. Lu, K.X. Su, Appl. Catal. A Gen. 304 (2006) 178–184.
[2] K. Takagi, T. Ishida, US Patent 3644526 (1972) to Sumitomo Chemical Company.
[3] P. Roffia, M. Padovan, G. Leofanti, M. Maria A, G.D. Alberti, G.R. Tauszik, US Patent 4794198 (1988) to Montedipe S.p.A.
[4] T. Sooknoi, V. Chitranuwatkul, J. Mol. Catal. A Chem. 236 (2005) 220–226.
[5] J.F. Knifton, J. Catal. 33 (1974) 289–298.
[6] S. Sakaguchi, Y. Nishiwaki, T. Kitamura, Y. Ishii, Angew. Chem. Int. Ed. 113 (2001) 228–230.
[7] T.T. J.N., J. Catal. 161 (1996) 570–576.
[8] X. Liang, Z. Mi, Y. Wang, L. Wang, X. Zhang, W. Wu, E. Min, S. Fu, J. Chem. Technol. Biotechnol. 79 (2004) 658–662.
[9] X. Liang, Z. Mi, Y. Wang, L. Wang, X. Zhang, T. Liu, Chem. Eng. Technol. 27 (2004) 176–180.
[10] GB Patent 860340 (1961) to DuPont.
[11] GB Patent 857,902 (1961) to DuPont.
[12] S. Isozaki, Y. Nishiwaki, S. Sakaguchi, Y. Ishii, Chem. Commun. (2001) 1352–1353.
[13] K. Yamaguchi, S. Shinachi, N. Mizuno, Chem. Commun. (2004) 424–425.
[14] P. Serna, M. López-Haro, J.J. Calvino, A. Corma, J. Catal. 263 (2009) 328–334.
[15] K.-i. Shimizu, T. Yamamoto, Y. Tai, A. Satsuma, J. Mol. Catal. A Chem. 345 (2011) 54–59.
[16] P.-L. Liu, H.-K. Zhang, S.-H. Liu, Z.-J. Yao, F. Hao, H.-G. Liao, K.-Y. You, H.-A. Luo, ChemCatChem (2013) 2932–2938.
[17] H. Tamon, H. Ishizaka, T. Araki, M. Okazaki, Carbon 36 (1998) 1257–1262.
[18] T. Otowa, Y. Nojima, T. Miyazaki, Carbon 35 (1997) 1315–1319.
[19] Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, Chem. Mater. 18 (2006) 4447–4464.
[20] Y. Huang, H. Cai, T. Yu, F. Zhang, F. Zhang, Y. Meng, D. Gu, Y. Wan, X. Sun, B. Tu, D. Zhao, Angew. Chem. Int. Ed. 46 (2007) 1089–1093.
[21] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 122 (2000) 10712–10713.
[22] C. Vercaemst, M. Ide, B. Allaert, N. Ledoux, F. Verpoort, P.V.D. Voort, Chem. Commun. (2007) 2261–2263.
[23] K. Lee, M. Kim, H. Kim, J. Mater. Chem. 20 (2010) 3791–3798.
[24] G.A. Somorjai, J.Y. Park, Top. Catal. 49 (2008) 126–135.