

PD SUPPORTED ON THE ACID FUNCTIONALIZED CARBON BLACK FOR THE HYDROGENATION OF CYCLOHEXENE: EFFECT OF CARBON PROPERTIES ON THE PD DISPERSION

Ji Sun Kim¹, Jae Ho Baek¹, Young Bok Ryu¹, Kyeong Ho Kim¹, Seong-Soo Hong², Jeong-Wook Park^{3, *}, Man Sig Lee^{1, *}

¹ Korea Institute of Industrial Technology [KITECH], Ulsan, South Korea

² Department of Chemical Engineering, Pukyong National University, Busan, Korea
Tel.: +82-(52)-980-6630 E-mail address: lms5440@kitech.re.kr

Abstract

The aim of this work is to be compared the effect of supports textural properties with pre-treatment method on dispersion of Pd particle. We have investigated the effects of chemical treatment on black carbon before and after being modified with HNO₃/H₂SO₄ by FT-IR, Raman spectroscopy. The Pd catalysts supported on black carbon having the different surface properties were characterized by XRD, FE-TEM and CO-chemisorption. The catalytic activities were tested in liquid hydrogenation of cyclohexene under mild condition. Black carbon pre-treated with 4M concentration of acid (BP4M) has higher I_D/I_G ratio of Raman and oxygen containing functional group from FT-IR. The Pd catalyst supported on BP4M is presented smaller particle size and higher dispersion. Also, the results of catalytic activities show that Pd/BP4M exhibits good performance, it gives cyclohexene conversion of 82.3 % under 5 bar, 40°C and 400rpm for 15min. From these results, the hydrogenation reaction on metal catalysts depends not only the nature of metal, but also on the particle size and metal dispersion on the support (carbon).

Keywords

black carbon, dispersion, hydrogenation, Pd/C, pre-treatment

Introduction

Catalytic hydrogenations are one of the most important processes of the chemical industry and selectivity is a timely issue.¹⁻³ The presence of carbon-carbon triple bond compounds in the alkene stream is undesirable in both chemical and polymer-grade propylene and ethylene, due to poisoning of the polymerization catalysts.⁴⁻⁷ The high cost of these catalysts makes it necessary to optimize their catalytic activity and to maximize the dispersion of the metal, since the rate of chemical reaction is, in general, proportional to the number of available surface metal atoms. Consequently, Expensive

hydrogenation catalysts employing noble metals are typically supported on materials such as alumina, silica, and zeolites. Palladium (Pd) is often the metal of choice in selective hydrogenation reactions and this is often partnered by carbon as a support due to its high surface area and low relative cost along with the ease by which the supported metal may be recovered.⁸⁻¹¹ Although the relative hydrophilicity of a carbon may be increased by treatment of the surface by reagents such as nitric acid and hydrogen peroxide which lead to increased density of surface oxygen containing functionalities, complete

miscibility with water is seldom achieved. In order to introduce more binding sites and obtain highly dispersed noble metal, surface functionalization of black carbon is carried out by chemical oxidation at defect sites of its surfaces. The oxygen functional groups, such as carboxyl group (–COOH), hydroxyl group (–OH), and carbonyl group (–C=O), is introduced due to the chemical oxidation with sulfuric and nitric acid. Functional groups on carbon surface contribute to high loading and uniform distribution of Pd particles. In this study, for the introduction of carboxyl groups (–COOH) onto the black carbon surface via an aggressive oxidation treatment with HNO₃ or HNO₃/H₂SO₄ mixture.

The aim of this work is to be compared the effect of supports textural properties with pre-treatment method on dispersion of Pd particle. We have investigated the effects of chemical treatment on black carbon before and after being modified with HNO₃/H₂SO₄ by FT-IR, Raman spectroscopy. The Pd/C catalysts prepared on support having the different surface properties were characterized by XRD, FE-TEM and CO-chemisorption. The catalytic activities were tested in hydrogenation of cyclohexene

Experiment details

Pristine black carbon (black pearl 2000) used in this study was purchased from Cabot Co., Ltd, which will be designated pristine BP. In typical experiment, acid functionalization of pristine BP process is as follow. The pristine BP was carried with sonication in a solution containing HNO₃ (69 %, Sigma Aldrich) and H₂SO₄ (95-97 %, Sigma aldrich) (1:1 vol) for 2 h at 25 °C with different concentration (2, 4, 8 M). Then, it was washed with distilled water until the washes pH of 5-6. The sample was dried overnight at 373 K. The pre-treated pristine BP were then ready for use in supporting of Pd nanoparticle, which will be designated as BP2M, BP4M and BP8M in this paper. The Pd/C catalysts were prepared by ion exchange in aqueous solution. The resulting material was filtered with filter paper and washed through distilled water until pH of 5-6, and then dried at 105 °C for 5 h

The characterization of the prepared Pd/C catalysts were conducted by nitrogen adsorption-desorption, XRD, FE-TEM and CO-Chemisorption. The hydrogenation of cyclohexene was carried out in a 100 mL capacity stainless steel autoclave equipped with temperature detector, pressure control and magnetically driven impeller.

Results and discussion

Throughout this review, we have shown the effect of supports textural properties with pre-treatment method on dispersion of Pd particle. The black carbon were functionalized by different concentration of acid in order to obtain materials with different surface properties. Density of carboxyl and total oxygen functional group strongly depend on the high concentration of acid solution whereas

carboxyl groups was dominantly introduced on the black carbon surface. The more detailed results of pretreated carbon and Pd/C catalyst shown Table 1. Also, the pretreatment causes decreasing graphitization. Because it causes a cutting off carbon double generating asymmetrical carbon and defect on the sidewall. When pretreated 4M concentration, the black carbon has the highest amount of oxygen functional group and I_D/I_G ratio. But, in more than 4M concentration, functional groups on the surface of black carbon are decreased because harsh acid oxidation inevitably causes sine structural damage of black carbon. Depending on pre-treatment concentration, carbon have different amount of functional groups. From these results, we confirmed that characteristics of Pd/C catalyst such as particle size and dispersion of Pd are influenced by density of oxygen functional group and disorder black carbon. Pd/BP4MB has smaller particle size and higher dispersion of Pd than Pd supported on pristine BP, BP2M, and BP4M. From these results, we confirmed that characteristic of Pd/C catalyst such as particle size and dispersion of Pd are influenced by density of oxygen functional group and disorder of black carbon. The catalyst were tested in the hydrogenation of cyclohexene to cyclohexane. The catalytic activity is in order of Pd/BP4M > Pd/BP2M > Pd/BP8M > Pd/pristine BP, Pd/4BP catalyst give the best results of cyclohexene conversion. The reason may be that smaller Pd particle size and higher Pd dispersion on the black carbon exhibited higher cyclohexene conversion. The hydrogenation reaction on metal catalysts depends not only on the nature of metal, but also on the particle size and metal dispersion on the support (carbon).

Table 1. Summary characterization of carbon and prepared Pd/C catalyst

Catalysts	Pd Size by TEM (nm)	CO gas adsorption (mmol/g)	Metal Dispersion (%)	Metallic Surface Area (m ² g ⁻¹)	Cyclohexene Conversion (%)
Pd/ Pristine BP	5-10	0.017	6.75	6.75	32.5
Pd/BP2M	2-3	0.0549	25.04	25.04	62.7
Pd/BP4M	2-3	0.0751	34.26	34.26	82.3
Pd/BP8M	10-15	0.0345	15.76	15.76	48.5

Conclusion

In this study, we confirmed that characteristics of Pd/C catalyst such as particle size and dispersion of Pd are influenced by density of oxygen functional group and disorder black carbon. Pd/BP4MB has smaller particle size and higher dispersion of Pd than Pd supported on pristine BP, BP2M, and BP4M. From these results, we confirmed that characteristic of Pd/C catalyst such as particle size and

dispersion of Pd are influenced by density of oxygen functional group and disorder of black carbon. The catalyst were tested in the hydrogenation of cyclohexene to cyclohexane. The catalytic activity is in order of Pd/BP4M > Pd/BP2M > Pd/BP8M > Pd/pristine BP, Pd/4BP catalyst give the best results of cyclohexene conversion. The reason may be that smaller Pd particle size and higher Pd dispersion on the black carbon exhibited higher cyclohexene conversion. The hydrogenation reaction on metal catalysts depends not only on the nature of metal, but also on the particle size and metal dispersion on the support (carbon).

Acknowledgments

This research was financially supported by Korea Institute of Industrial Technology (KITECH) and Ulsan city, "Climate Change Green Technology on Support Project [Matching Fund]" and Ministry of Strategy and Finance "Corporate demand R&D (Super IP) (Project No. JB15050).

References

1. G. Neri, M.G. Musolino, C. Milone, A.M. Visco, A. Di Mario, *J. Mol. Catal. A: Chem.* 95, 235 (1995).
2. G.C. Torres, E.L. Jablonski, G.T. Baronetti, A.A. Castro, S.R. De Miguel, O.A. Scelza, M.D. Blanco, M.A. Pena-Jimenez, J.L.G. Fierro, *Appl. Catal. A: Gen.* 161, 213 (1997).
3. D.S. Cameron, S.J. Cooper, I.L. Dogson, B. Harrison, J.W. Jenkins, *Catal. Today* 7, 113 (1990).
4. J. Jia, Y. Wang, E. Tanabe, T. Shishido, K. Takehira, *Micropor. Mesopor. Mater.* 57, 283 (2003).
5. H.E. van Dam, L.J. Wisse, H. van Bekkum, *Appl. Catal.* 61, 187 (1990).
6. J. S. Kim, J. H. Baek, M. H. Kim, S. S. Hong, M. S. Lee, *Appl. Chem. Eng.* 24, 650 (2013).
7. Y. Sun, R.N. Landau, J. Wang, C. LeBlond, D.G. Blackmond, *J. Am. Chem. Soc.* 118, 1348 (1996).
8. J.A. Anderson, A. Athawale, F.E. Imrie, F.-M. McKenna, A. McCue, D. Molyneux, K. Power, M. Shand, R.P.K. Wells, *J. Catal.* 270, 9 (2010).
9. Y. Zhang, K.J. Smith, *Catal. Today* 77, 257 (2002).
10. S. Takenaka, H. Ogihara, K. Otsuka, *J. Catal.* 208, 54 (2002).
11. T.V. Choudhary, C. Sivadinarayana, C.C. Chusuei, A. Klinghoffer, D.W. Goodman, *J. Catal.* 199, 9 (2001).