Catalysis Communications 12 (2011) 1071–1074

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

Highly selective palladium supported catalyst for hydrogenation of phenol in aqueous phase

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ARTICLE INFO

Article history:
Received 24 November 2010
Received in revised form 16 March 2011
Accepted 19 March 2011
Available online 26 March 2011

Keywords:
Selective hydrogenation
Cyclohexanone
Metal nanoparticles
High surface area alumina

ABSTRACT

Hydrogenation of phenol to cyclohexanone in aqueous phase, under mild conditions, has been carried out using palladium on different supports such as hydroxyapatite (HA), carbon (C), alumina (γ-Al_2O_3) and Al_2O_3-CWE synthesized with high surface area. High activity (100%) and selectivity (98%) to cyclohexanone was obtained using Pd/ Al_2O_3-CWE catalyst in 50 min under mild reaction conditions.

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1. Introduction

Catalytic hydrogenation of phenol to cyclohexanone is a reaction of potential industrial interest for the production of caprolactam for Nylon-6 and adipic acid for Nylon-66 [1]. The hydrogenation produces cyclohexenol (step I), as intermediate product, that subsequently gives cyclohexanol (via hydrogenation, step III), or cyclohexanone (via isomerization, step II) which can be converted into cyclohexanol via hydrogenation (step IV) (Fig. 1). The hydrogenation of phenol has been mainly carried out in vapor phase with supported palladium catalysts, at high hydrogen pressure and temperatures which usually causes catalyst deactivation by cooking generating undesirable by-products that lower the yield and complicate the separation [2–14]. Gas–liquid reactions with palladium [15,16] rhodium [16,17], and ruthenium catalysts [16,18], working in super critical carbon dioxide, have advantages for increasing solubility of reactant gases or easy separation of catalyst and products [19]. However the reaction conditions are high H_2 and CO_2 pressure, 10 Mpa H_2 and 12 Mpa CO_2 or 10 Mpa H_2 and 4 Mpa CO_2.

Several reports on the hydrogenation of phenol in vapor phase, have suggested that the catalytic activity and selectivity for cyclohexanone depend on the method used for catalyst preparation, metal loading [3–5,10], nature of support (acidity/basicity), [2,7,9] inclusion of promoters (alkali metals/alkaline earth metals and lanthanides) [3,11], the nature of the palladium catalyst precursor [9], alloying with a second metal [4] and concentration of the reactants [2,3,7]. However, contradictory results on the role of the different variables have been reported. For instance some reports have proposed that supports with acidic properties [2,9] are more selective for formation of cyclohexanone than others which presents basic properties. Others suggest that the basic nature of the support [3,7] or adding calcium to reduce the surface acidity increases cyclohexanone selectivity [11]. It appears that the final results obtained can also be strongly influenced by the operation conditions.

The hydrogenation of phenol in liquid phase presents some important advantages in comparison with gas phase, such as increasing catalyst life and quality of the reaction products [20]. Curiously, a limited amount of work has been reported on the hydrogenation of phenol in liquid phase [21–25]. Gonzalez-Velasco et al. [21] have prepared various Pd/Al_2O_3 catalysts for the hydrogenation of phenol in cyclohexane as solvent under 10–30 bars and 160 °C–200 °C reaction temperature. However it would be much better from an environmental point of view to replace the organic solvent with water. This has been done by Goettmann et al. [23] who performed the hydrogenation of phenol in aqueous phase to produce cyclohexanone. The authors conclude that Pd supported on specially synthesized carbons with strong hydrophilic properties work better than when the support was alumina, and consider this a key variable that determines activity and selectivity. This is interesting if one takes into account that hydroxylated aluminas are also quite hydrophilic. Nevertheless it should also be considered that the support must also have an important impact on the metal particle size which, in turn, must influence catalyst activity and selectivity.

We will present here that it is possible to obtain better activities, with excellent selectivities for hydrogenation of phenol in aqueous phase by preparing large surface area mesoporous aluminas with

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doi:10.1016/j.catcom.2011.03.026

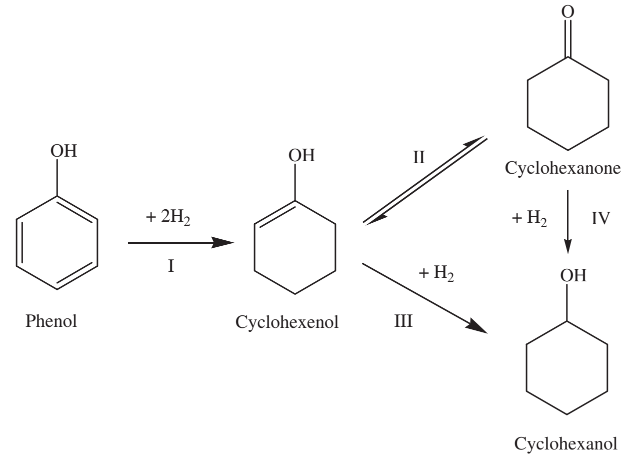

Fig. 1. Reaction showing steps in the hydrogenation of phenol.

small Pd metal nanoparticles. In the first part of the work, and in order to elucidate the influence of the support on hydrogenation of phenol in aqueous phase, supports of different nature: hydroxyapatite (HA), carbon (C), alumina (γ-Al_2O_3, acidic properties) and alumina with high surface area (Al_2O_3-CWE), have been used. Then, catalytic properties have been related not only with the nature of the support but with the size of the Pd nanocrystals obtained on the different carriers.

2. Experimental

2.1. Materials

Phenol, cyclohexanone, cyclohexanol, propylene oxide, $AlCl_3$, and $PdCl_2(PhCN)_2$ were purchased from Sigma-Aldrich and used as received. Acetone, etanol (Scharlau), and water (Milli-Q, Millipore) were used as solvents, whereas hydrogen 5.0 (Abelló Linde S.A., 99.999%) was used as reducing agent. The carbon support was purchased from Aldrich with 1600 $m^2\,g^{-1}$ surface area while γ-Al_2O_3 (238 $m^2\,g^{-1}$) was obtained with bohemite from Condea at 500 °C for 10 h. Hydroxyapatite with 98 $m^2\,g^{-1}$ surface area was prepared following the procedure reported in Ref. [26]. For comparative purposes the commercial catalysts: 5% Pd/C-com (palladium on activated charcoal from Fluka), 10% Pd/C-com (palladium on activated charcoal from Fluka) and 10% Pd/Al_2O_3-com (palladium on activated alumina from Aldrich) were also used.

The synthesis of high surface area Al_2O_3-CWE using propylene oxide in ethahol/water (50/50) has been reported previously [27]. In a typical synthesis, $AlCl_3$ was dissolved in 20 mL of ethahol/water (50/50) in a plastic glass. Then, propylene oxide was added and the resulting solution stirred for 10 min, and allowed to form the gel by stopping stirring. The aged gel (24 h) was washed in a bath of ethanol for 24 h. The gel was lyophilizated for 8 h to get alumina aerogel, which was used without calcining.

Incorporation of palladium on different supports was performed by the impregnation method with $PdCl_2(PhCN)_2$ as the source of Pd, following the experimental procedure detailed in Ref. [26].

2.2. Catalytic experiments

A reinforced glass batch reactor (8 mL) was used to carry out the liquid phase hydrogenation. Phenol (100 mg, 1.06 mmol) dissolved in 5 mL of water was placed into the reactor followed by catalyst addition (see the amount of catalyst in Table 1). The reactor was purged two times with hydrogen and then pressurized with 5 bars of hydrogen. The reaction mixture was heated up to 100 °C and stirred at 500 rpm. The products were periodically extracted (100 µL samples), analyzed and identified by GC and GC–MS.

3. Results and discussion

Pd (1.5 wt.%) was supported on hydroxyapatite (HA) by impregnation with an acetone solution of $PdCl_2(PhCN)_2$ [26]. The same method of impregnation was applied to prepare Pd/C (Pd content: 1.5 wt.%), Pd/γ-Al_2O_3 (Pd content: and 0.2 wt.%) and Pd/Al_2O_3-CWE (Pd content: 1.5 wt.%). The catalyst Pd/Al_2O_3-CWE presents higher surface area (406 $m^2\,g^{-1}$) than Pd/γ-Al_2O_3 and Pd/HA (237 $m^2\,g^{-1}$ and 98 $m^2\,g^{-1}$, respectively). The average pore diameters are 43 , 41 and 57 for Pd/Al_2O_3-CWE, Pd/γ-Al_2O_3 and Pd/HA, respectively. The crystal size of the supported Pd was determined by TEM, and representative pictures with the corresponding size distribution are given in Figs. 2 and 3 for Pd/γ-Al_2O_3 and Pd/Al_2O_3-CWE and in supplementary data Figs. A3 and A4 for Pd/HA and Pd/C. As can be seen there, both catalysts Pd/γ-Al_2O_3 and Pd/Al_2O_3-CWE show narrow crystallite size distribution with average palladium crystal sizes of 4.6 and 5 nm, respectively.

The catalysts were tested for the hydrogenation of phenol in aqueous media under mild conditions, as described in Experimental. Moreover, the catalysts prepared here were compared with the commercially available 5% Pd/C-com, 10% Pd/C-com and 10% Pd/Al_2O_3-com, for the hydrogenation of phenol at 5 bars of hydrogen and 100 °C, and the results obtained are showed in Fig. 4 and Table 1.

Results from Fig. 4 clearly show that the catalysts synthesized here give better activity and selectivity to cyclohexanone than the commercially prepared Pd on carbon and alumina. Moreover, Pd supported over alumina and hydroxyapatite, was more active and more selective to cyclohexanone than the catalysts supported on

Table 1
Comparative catalytic performance of different palladium catalyst.

Conversion[a](%)								Selectivity (%)	
Catalyst	Pd[b] (wt.%)	$m_{catalyst}$ (g)	10 min	30 min	50 min	90 min	120 min	C=O cyclohexanona	C–OH cyclohexanol
Pd/Al_2O_3-CWE	1.5	0.188	70	96	100	100	100	98	
Pd/γ-Al_2O_3	0.2	1.41	26	30	37	40	58	100	3
Pd/γ-Al_2O_3	1.5	0.188	35	89	100	100	100	97	–
Pd/Al_2O_3-com	10	0.028	8	31	60	100	100	78	3
Pd/HA	1.5	0.188	21	87	100	100	100	97	2
Pd/C	1	0.282	17	46	73	100	100	98	2
Pd/C-com	5	0.056	5	13	28	80	100	74	26
Pd/C-com	10	0.028	9	21	35	61	100	86	14

Reaction conditions: phenol (100 mg and 1.06 mmol) dissolved in water (5 mL) in the presence the solid catalyst, stirred in a glass reactor (8.0 mL), pressurized with H_2 (5 bars) and heated to 100 °C.

[a] The conversion was determined by GC analysis and the products identified by GC–MS with the external standard method.

[b] wt.% of palladium measured by inductively coupled plasma (ICP) chemical analysis.

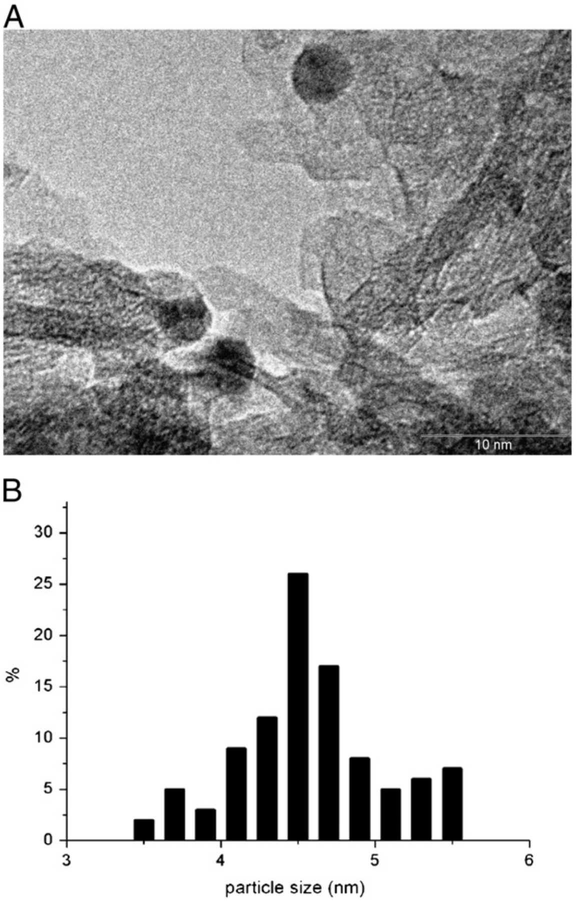

Fig. 2. A) TEM image of 1.5 wt.% Pd/γ-Al_2O_3 and B) Pd particle size distribution of 1.5 wt.% Pd/γ-Al_2O_3.

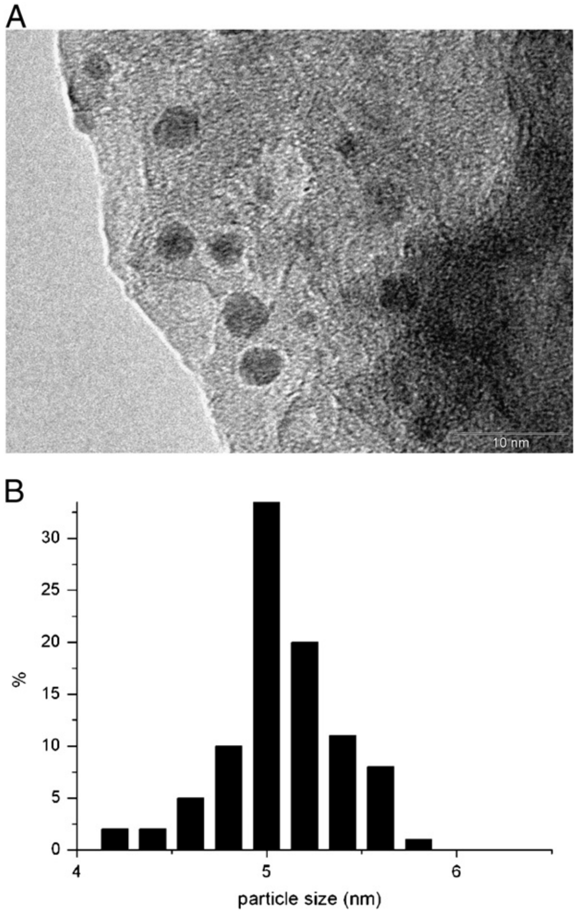

Fig. 3. A) TEM image of 1.5 wt.% Pd/Al_2O_3-CWE and B) Pd particle size distribution of 1.5 wt.% Pd/Al_2O_3-CWE.

carbon. From these results, and in a first approximation, one could conclude that the nature of the support plays an important role on activity and selectivity of Pd catalysts for the hydrogenation of phenol. Indeed, results reported on the mechanism of the reaction [3] seem to indicate that the reaction occurs between phenol adsorbed on the support and hydrogen activated on the metal. If this is so, it seems logical that, for a given support, the larger the metal dispersion the higher should be the activity. The palladium supported on Al_2O_3 with high surface area showed the highest activity (see Fig. 4) with 98% of selectivity for cyclohexanone and 100% of conversion in 50 min of rection. This catalyst presents an even higher activity than Pd/on hydrophilic hydrothermal carbon which was a good catalyst recently presented by Goettmann et al. [23], which gave 99% conversion and 95% selectivity to cyclohexanone after 20 h reaction time.

Since both the support and surface metal atoms should influence the final catalyst activity, the metal dispersion was determined from H_2 chemisorption measurement for each catalyst (see Table 2). The phenol hydrogenation activity (TOF) increased with increasing Pd dispersion and the selectivity to cyclohexanone increases from almost 78% (for Pd/Al_2O_3-com) to 98% (for Pd/Al_2O_3-CWE) with Pd dispersion of 18.5 and 63.7, respectively. The activity is a direct function of the metal dispersion (see Fig. A5 in supplementary data), and consequently the highest activity (TOF = 0.15) for Pd/Al_2O_3-CWE can be attributed to the high metal dispersion, as a consequence of the higher surface area of the already adequate support. The phenol hydrogenation activity for Pd/Al_2O_3-CWE in aqueous phase is similar to the results obtained by Mahata and Vishwanathan [9] with different Pd/Al_2O_3, working in vapor phase.

4. Conclusions

In conclusion we have presented that taking into account a catalyst reactivity model wherein phenol adsorbs on the support and H_2 is activated on the metal, it is possible to achieve practically 100% selectivity to cyclohexanone at 100% conversion by maximizing the support metal interface. This is achieved with a high surface area hydrophilic alumina support with small nanocrystallites of Pd.

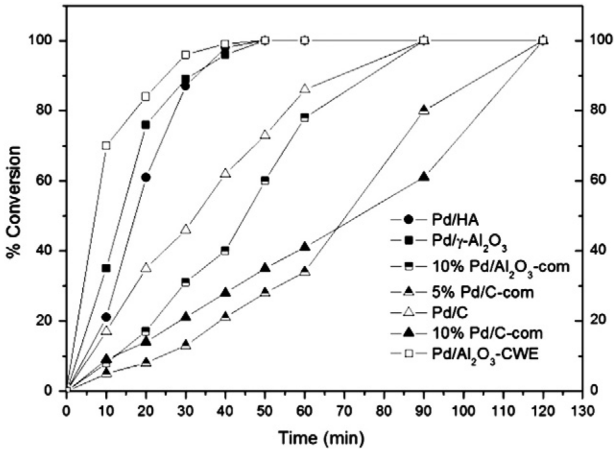

Fig. 4. Conversions of phenol versus reaction time with the different catalysts.

Table 2
H_2 chemisorption properties, content and TOF of palladium supported catalysts.

Catalyst	Pd[a] (wt.%)	Pd dispersion[b] (%)	Metal area[b] (m^2/g cat)	Metal area[b] (m^2/g Pd)	No. of Pd[b] sites g (cat) $^{-1}$ ($\times 10^{19}$)	TOF[c] (s^{-1})
Pd/Al_2O_3-CWE	1.5	63.7	4.2	283.7	5.405	0.15
Pd/γ-Al_2O_3	1.5	43.9	2.9	195.8	3.725	0.09
Pd/Al_2O_3-com	10	18.5	8.2	82.4	10.965	0.02
Pd/HA	1.5	22.3	1.5	99.5	1.892	0.04

[a] wt.% of palladium measured by inductively coupled plasma (ICP) chemical analysis.
[b] Calculated from H_2 chemisorption.
[c] Number of phenol molecules converted per surface Pd atom per second.

Acknowledgements

Financial support by CONSOLIDER INGENIO 2010 (project Multicat) is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.03.026.

References

[1] World Nylon 6 & 66 Supply/Demand Report, PCI-Fibers and Raw Materials, Seaford, UK, 1998.
[2] A.K. Talukdar, K.G. Bhattacharyya, Appl. Catal. A Gen. 96 (1993) 229.
[3] G. Neri, A.M. Visco, A. Donato, C. Milone, M. Malentacchi, Appl. Catal. A Gen. 110 (1994) 49.
[4] S.T. Srinivas, L.J. Lakshmi, P.K. Rao, Appl. Catal. A Gen. 110 (1994) 167.
[5] S. Narayanan, K. Krishna, Appl. Catal. A Gen. 147 (1996) L253.
[6] S. Narayanan, K. Krishna, Appl. Catal. A Gen. 174 (1998) 221.
[7] Y.Z. Chen, C.W. Liaw, L.I. Lee, Appl. Catal. A Gen. 177 (1999) 1.
[8] P. Claus, H. Berndt, C. Mohr, J. Radnik, E.-J. Shin, M.A. Keane, J. Catal. 192 (2000) 88.
[9] N. Mahata, V. Vishwanathan, J. Catal. 196 (2000) 262.
[10] N. Mahata, K.V. Raghavan, V. Vishwanathan, C. Park, M.A. Keane, Phys. Chem. Chem. Phys. 3 (2001) 2712.
[11] S. Scire, S. Minico, C. Crisafulli, Appl. Catal. A Gen. 235 (2002) 21.
[12] S. Velu, M.P. Kapoor, S. Inagaki, K. Suzuki, Appl. Catal. A Gen. 245 (2003) 317.
[13] L.M. Sikhwivhilu, N.J. Coville, D. Naresh, K.V.R. Chary, V. Vishwanathan, Appl. Catal. A Gen. 324 (2007) 52.
[14] K.V.R. Chary, D. Naresh, V. Vishwanathan, W. Ueda, Catal. Commun. 8 (2007) 471.
[15] V. Arunajatesan, B. Subramaniam, K.W. Hutchenson, F.E. Herkes, Chem. Eng. Sci. 56 (2001) 1363.
[16] C.V. Rode, U.D. Joshi, O. Sato, M. Shirai, Chem. Commun. (2003) 1960.
[17] K.V.R. Chary, D. Naresh, V. Vishwanathan, W. Ueda, Catal. Commun. 9 (2008) 362.
[18] A.M.R. Galletti, C. Antonietti, I. Longo, G. Capannelli, A.M. Venezia, Appl. Catal. A Gen. 350 (2008) 46.
[19] Chemical Synthesis Using Supercritical Fluids, in: P.G. Jessop, W. Leitner (Eds.), Wiley, New York, 1999.
[20] M.M. Sharma, Chem. Eng. Sci. 38 (1983) 21.
[21] J.R. González-Velasco, M.P. González-Marcos, S. Arnaiz, J.I. Gutiérrez-Órtiz, M.A. Gutiérrez-Órtiz, Ind. Eng. Chem. Res. 34 (1995) 1031.
[22] E.D. Díaz, A.F. Mohedano, L. Calvo, M.A. Gilarranz, J.A. Casas, J.J. Rodríguez, Chem. Eng. J. 131 (2007) 65.
[23] P. Makowshi, R.D. Cakan, M. Antonietti, F. Goettmann, M.-M. Titirici, Chem. Commun. (2008) 999.
[24] H. Li, J. Liu, H. Li, Mater. Letter. 62 (2008) 297.
[25] E.D. Díaz, A.F. Mohedano, L. Calvo, M.A. Gilarranz, J.A. Casas, J. Rodríguez, Green Chem. 10 (2008) 939.
[26] A. Abad, C. Almela, A. Corma, H. García, Tetrahedron 62 (2006) 6666.
[27] T.F. Baumann, A.E. Gash, S.C. Chinn, A.M. Sawvel, R.S. Maxwell, J.H. Satcher, Chem. Mater. 17 (2005) 395.