A study of nitrobenzene hydrogenation over palladium/carbon catalysts

Elaine A. Gelder[a], S. David Jackson[a,*], and C. Martin Lok[b]
[a] *Department of Chemistry, The University, Glasgow G12 8QQ, Scotland*
[b] *Synetix, P.O. Box 1, Belasis Avenue, Billingham, Cleveland TS23 1LB, UK*

Received 27 August 2002; accepted 29 August 2002

The hydrogenation of nitrobenzene has been studied over three palladium/carbon catalysts using methanol and isopropanol as solvents. A solvent and palladium particle size effect have both been observed, with the nature of the particle size effect dependent upon the solvent. This may be related to a change in the rate-determining step.

KEY WORDS: palladium; nitrobenzene; hydrogenation; carbon; aniline; particle size effect.

1. Introduction

The catalytic hydrogenation of nitrobenzene is commonly employed as a standard reference reaction for testing and comparing the activity of hydrogenation catalysts for a range of applications [1–5]. In addition, it is an important industrial reaction used in the commercial production of aniline for use in the polyurethane industry [6]. However, although there is extensive literature available citing the use of this reaction as a test of catalyst activity, there are relatively few publications investigating the hydrogenation reaction. A reaction mechanism for nitrobenzene hydrogenation was first proposed by Haber in 1898 and has been widely accepted since [7]. Unfortunately, this mechanism is still not well understood and has never been thoroughly investigated. For example, in the industrial process the catalysts are prone to deactivation, yet no deactivation mechanism has been delineated. This study forms part of a wider investigation into the mechanistic scheme for the hydrogenation of nitrobenzene and into the deactivation of the catalysts. Initial studies have focused upon palladium metal, which has been employed extensively for the hydrogenation of nitrobenzene [8–10]. Three activated carbon supports were used to examine any support effect. In addition, two different solvents were employed to ascertain the influence of reaction solvent on the reaction mechanism.

2. Experimental

All catalysts were prepared by impregnation. Three different powdered activated carbon supports were used: Norit CN1 (surface area 1400 $m^2 g^{-1}$), Norit CA1 (surface area 1400 $m^2 g^{-1}$) and Norit SX Ultra (surface area 1200 $m^2 g^{-1}$). Sufficient palladium nitrate solution (PGP, assay 10.123% Pd), to produce a palladium loading of 3%, was added to each support. The resulting suspensions were dried and calcined at 423 K for 3 h.

The dispersion of each catalyst was measured by CO chemisorption. Taking a CO:Pd ratio of 1:2 the dispersions shown in table 1 were calculated and from these an approximate metal particle size determined assuming a spherical model.

Nitrobenzene hydrogenation was carried out in a Buchi stirred autoclave. The reactor design allowed regulation of reaction temperature, hydrogen gas pressure, and stirring speed. In addition, it also allowed *in situ* reduction of the catalyst prior to the reactant being added. The catalyst (0.10 g) was added to the reactor along with the reaction solvent (280 ml methanol or isopropanol (IPA)). The autoclave was then purged with nitrogen. The catalyst was reduced in a flow of hydrogen (30 $cm^3 min^{-1}$). With hydrogen being sparged through the solvent the mechanical stirrer was set to 300 rpm and the temperature increased to 323 K. The temperature was held for 30 min. The hydrogen flow and stirring were then stopped and nitrobenzene (17 ml, 0.166 moles) added *via* an injection port. Following purging with nitrogen, the system was pressurized with hydrogen (5 barg). The reaction commenced when the

Table 1.

Catalyst	Dispersion (%)	Average particle size (nm)
Pd/CN1	9	12
Pd/CA1	13	9
Pd/CSXU	42	3

---

[*] To whom correspondence should be addressed.

1011-372X/02/1200-0205/0 © 2002 Plenum Publishing Corporation

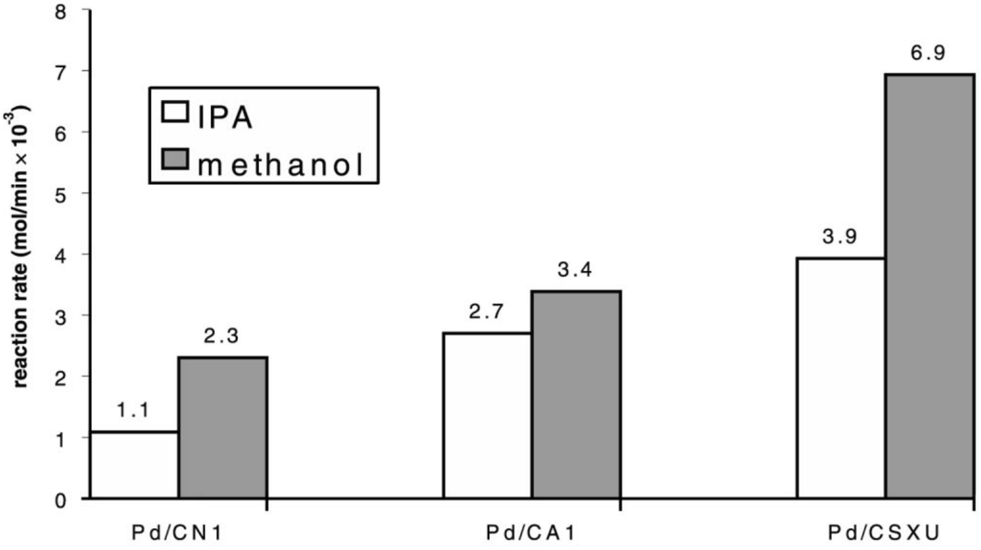

Figure 1. Nitrobenzene hydrogenation over Pd/CN1 in IPA and methanol.

stirrer was switched on. A temperature of 323 K was used for all reactions. The stirrer speed was set at 1000 rpm. No variation in hydrogenation rate was observed over a range of stirrer speeds (800–1500 rpm) indicating the absence of mass-transfer control. Analysis of the reaction mixture was performed by GC using a Chrompack CP 9000, with an FID detector fitted with a 30 m FFAP column.

3. Results

The three catalysts Pd/CN1, Pd/CA1, and Pd/CSXU were used to hydrogenate nitrobenzene under the conditions described in the experimental section using both methanol and IPA as the reaction solvent. The reaction rates were obtained by monitoring the hydrogen uptake. Liquid phase analysis confirmed the presence of only nitrobenzene and aniline as reactant and product: no other species were detected. All three catalysts, in both reaction media, show a linear uptake of hydrogen over the duration of the experiment. However, with each catalyst the reaction proceeds more rapidly in methanol than in IPA. The results are displayed in figures 1–3 and a comparison of the initial rates in figure 4.

4. Discussion

The difference in reaction rate when hydrogenation is performed in methanol or IPA indicates that a solvent effect is in operation (figures 1–3). From the initial rates of hydrogenation for each catalyst (figure 4) it is evident that the most disperse palladium catalyst with the smallest metal particles (Pd/CSXU) gives the highest activity whereas the least disperse catalyst (Pd/CN1) displays the slowest rate. In addition, the difference in rate between the two solvents is of a comparable magnitude for each catalyst. However, when the turnover frequency of nitrobenzene to aniline was calculated for each catalyst a more complex picture was seen (figure 5). Although a higher rate of reaction in methanol compared to IPA was confirmed, the graph demonstrates that catalyst Pd/CA1 is the most efficient catalyst in terms of the turnover frequency. Therefore, despite demonstrating the highest reaction rate, catalyst Pd/CSXU is shown to be the least effective in terms of the number of nitrobenzene molecules hydrogenated per metal atom. This suggests that the reaction is structure-sensitive. Examination of the results observed using methanol as the solvent reveals that Pd/CN1 and

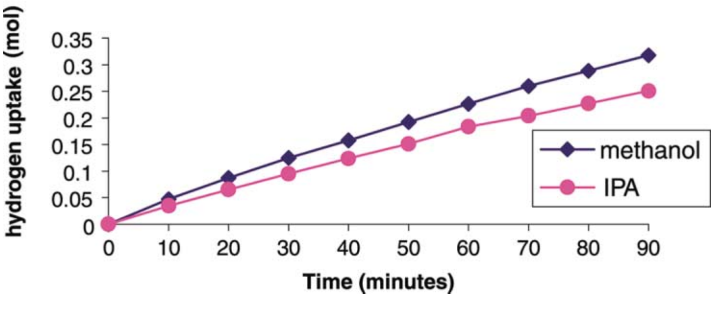

Figure 2. Nitrobenzene hydrogenation over Pd/CA1 in IPA and methanol.

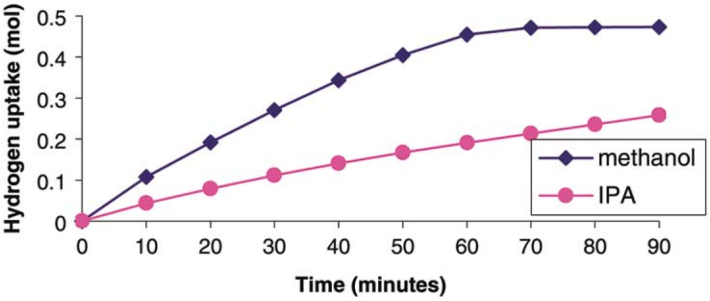

Figure 3. Nitrobenzene hydrogenation over Pd/CSXU in IPA and methanol.

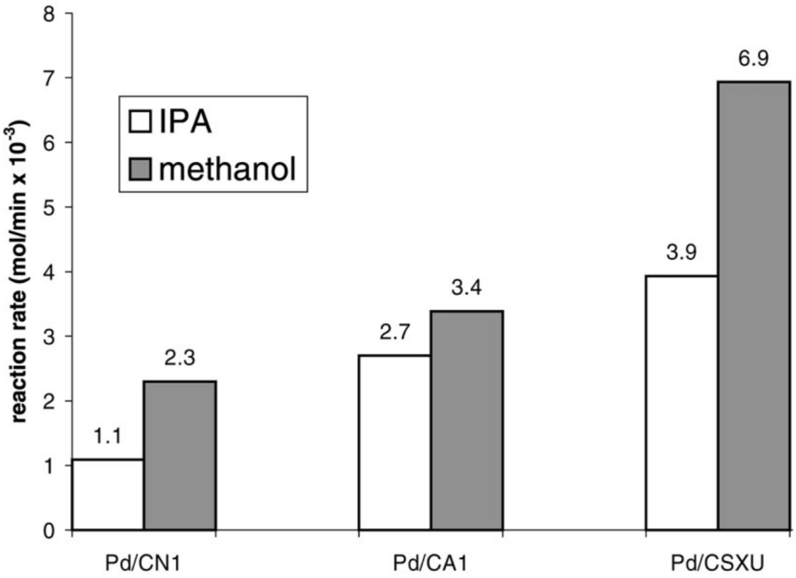

Figure 4. Comparison of rate of reaction in IPA and methanol.

Pd/CA1, the catalysts with the larger palladium particles, exhibit similar turnover frequencies, whereas Pd/CSXU, which has a smaller metal particle size, has a significantly reduced turnover frequency. Therefore, it can be postulated that, in a methanol solvent, the preferred sites for nitrobenzene hydrogenation are situated mainly on the plane surfaces of the catalysts as opposed to edges or corners.

When IPA is used as the solvent, however, a different pattern in turnover frequency is observed. Catalyst Pd/CA1 displays a significantly higher turnover frequency than Pd/CN1 or Pd/CSXU, showing that in IPA an optimal palladium crystallite size exists. Obviously with only three systems it is impossible to tell whether the size of ~9 nm is actually the maximum, but clearly a maximum is present. It is slightly surprising that a

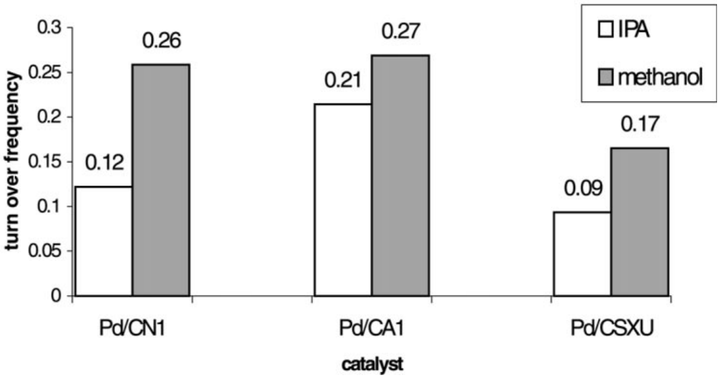

Figure 5. Comparison of turnover frequencies.

particle size effect should be seen, as from the work of van Hardeveld and Hartog [11] the surface should be changing very little between 9 nm and 12 nm. Hence we must also consider that the support could be influencing the reactivity.

This decrease in reaction rate on going from methanol to IPA is consistent with previous studies by Kochetova *et al.* [12], where reaction proceeded at a faster rate in ethanol than IPA. It was postulated that this may be due to greater charge stabilization of the intermediates in the reaction mechanism and a change of the rate-limiting step from the hydrogenation of nitrobenzene to the hydrogenation of nitrosobenzene. A change in mechanism such as this may explain the difference observed in the turnover frequency for the three catalysts in the different solvents. When methanol is employed as the reaction solvent, a reduction in turnover frequency is observed as the particle size falls below a certain level. As discussed above, this is suggestive of selective adsorption of nitrobenzene on the plane surfaces of the metal crystallites. An alteration in the rate-determining step to one involving nitrosobenzene will also mean a change in the preferred hydrogenation site. Consequently, the ability of particle size and shape to optimize these sites will also differ.

5. Conclusions

In summary, this study has utilized palladium supported on three separate activated carbon powders to hydrogenate nitrobenzene using two solvents, methanol and IPA. A significant solvent effect has been demonstrated with hydrogenation proceeding more rapidly in methanol than in IPA. In addition, a metal particle size effect has also been observed. The particle size effect is also sensitive to the solvent and may be related to a potential change in the rate-determining step.

Acknowledgments

The authors would like to thank L. Shaw for the preparation of the catalysts and the support of EPSRC and Synetix for one of us (E.A.G.).

References

[1] N.J. Jebarathinam, M.E. Eswaramoorthy and V. Krishnasamy, Studies Surf. Sci. Catal. 113 (1998) 1039.
[2] C. Li, Y.-W. Chen and W.-J. Wang, Appl. Catal. A 119 (1994) 185.
[3] X. Fang, S. Yao, Z. Qing and F. Li, Appl. Catal. A 161 (1997) 129.
[4] M.C. Macias Perez, C. Salinas Martinez de Lecca and A. Linares Solano, Appl. Catal. A 151 (1997) 461.
[5] J. Wisniak and M. Klein, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 44.
[6] K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry*, 3rd edition (VCH, Weinheim, 1997) p. 375.
[7] F. Haber, Zeit. Electrochem. 4 (1898) 506.
[8] A. Metcalfe and M.W. Rowden, J. Catal. 22 (1971) 30.
[9] V. Holler, D. Wegricht, I. Yuranov, L. Kiwi-Minsker and A. Renken, Chem. Eng. Technol. 23 (2000) 251.
[10] X. Yu, M. Wang and H. Li, Appl. Catal. A. 202 (2000) 17.
[11] R. van Hardeveld and F. Hartog, Adv. Catal. 22 (1972) 75.
[12] L.B. Kochetova, T.G. Volkova and M.V. Klyuev, Petrol. Chem. 40 (2000) 371.