

Electronic Modifications in Supported Palladium Catalysts

B.L. Mojet^a, M.J. Kappers^a, J.C. Muijsers^b, J.W. Niemantsverdriet^b, J.T. Miller^c, F.S. Modica^c,
and D.C. Koningsberger^a

^a Debye Institute, Laboratory of Inorganic Chemistry, Utrecht University, P.O. Box 80083,
3508 TB Utrecht, The Netherlands

^b Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB
Eindhoven, The Netherlands

^c Amoco Oil Company, Amoco Research Center, 150 W. Warrenville Rd., Naperville, Illinois
60566, USA

SUMMARY

XPS and IR spectroscopy indicate that the electron density of the supported metal clusters in Pd/LTL catalysts is a function of the support acidity/alkalinity. In addition, the neopentane and propane hydrogenolysis TOF's increase with increasing support acidity from alkaline to acidic. The changes in spectroscopic and catalytic properties are due to electron deficient Pd on acidic supports, as previously proposed, and electron rich Pd on alkaline supports.

1. INTRODUCTION

Since the early work of Dalla Betta and Boudart ^[1], numerous studies have reported enhancements in the specific rate for Pt or Pd on acidic supports compared to neutral supports for benzene hydrogenation ^[2,3], propane hydrogenolysis ^[4,5], and neopentane hydrogenolysis and isomerisation ^[1,5-7]. The rate enhancement on acidic supports was proposed to be due to electron deficient metal particles ^[1]. The electron deficient nature of acidic supported metal clusters has been studied by infrared spectroscopy ^[8,9], electron spin resonance (ESR) ^[10], X-ray photoelectron spectroscopy (XPS) ^[10-14], and X-ray absorption near-edge spectroscopy (XANES) ^[15-17].

Several explanations have been proposed in order to account for metal electron deficiency. One of the explanations suggests a partial electron transfer from the metal to the support ^[1]. However, most of the oxide supports with which the effect has been observed are non-reducible insulators, whose ability to accommodate extra electronic charge is limited. Alternatively, Sachtler, et. al., have suggested that Pd in acidic zeolite Y can form positively charged Pd_n-H⁺ adducts ^[6-7,14,18], where the proton charge is delocalised over the palladium clusters. Finally, Van Santen and co-workers have proposed that a small metal cluster is polarised by a nearby cation. Calculations indicate that electrons are attracted by metal atoms near the cations, leading to electron-deficient metal atoms that are at the opposite side of the cations ^[19-20].

Previous work in our laboratories has shown that the catalytic properties of Pt/LTL are affected by metal-support interactions with alkaline as well as acidic supports^[5]. These interactions are probably similar in nature, forming a gradual change from acidic, through neutral, to alkaline supports. In this study Pd on zeolite-L supports, ranging from acidic to alkaline is examined, using IR and XPS spectroscopy and hydrogenolysis of neopentane and propane.

2. EXPERIMENTAL

2.1. Catalyst preparation

The acidity of the K-LTL zeolite support was varied by either impregnating a commercial LTL zeolite with KNO_3 or exchanging with NH_4NO_3 to give K/Al ratios ranging from 0.55 to 1.45. Each LTL-zeolite was calcined at 400°C and analysed for K and Al. The supports are designated LTL (x.xx), with x.xx representing the K/Al molar ratio. Palladium was added by incipient wetness impregnation using an aqueous solution of tetra-amine palladium (II) nitrate, followed by drying at 125°C . The elemental analysis of the catalysts is given in Table 1.

2.2. Neopentane and propane hydrogenolysis

The conversion of neopentane or propane was conducted at atmospheric pressure in a fixed-bed reactor using either 1.25 vol% neopentane or 3.78 vol% propane in H_2 . The catalysts were pre-reduced at the reaction temperature and conversion was adjusted to between 0.5 and 5% by varying space velocity.

The specific activity of Pd/LTL (1.45) was too low to measure at the same temperature as Pd/LTL (0.55). Therefore, the activities of Pd/LTL(1.01) and Pt/LTL(1.45) were determined at higher temperature and the activity of Pd/LTL(1.45) was estimated at lower temperature, assuming the ratios of activity are the same at low and high temperature. The Turnover Frequency (TOF) is calculated based on volumetric CO chemisorption.

2.3. XPS

The XP spectra were measured using a VG ESCALAB-200 spectrometer with a Mg $\text{K}\alpha$ X-ray source. Base pressure of the system was below 1.10^{-9} mbar. Energies were calibrated using the C 1s peak (284.6 eV). The catalysts were reduced at 300°C , followed by cooling under nitrogen to avoid formation of palladium hydrides. The samples were ground under nitrogen atmosphere and pressed into indium foil. They were transported to the spectrometer in a transfer vessel filled with nitrogen to prevent contact with air.

Table 1
Elemental Analysis

Catalyst (K/Al molar ratio)	Wt% Pd	Wt% Al	Wt% K
Pd/LTL (0.55)	1.74	8.7	6.9
Pd/LTL (1.01)	1.71	8.7	12.8
Pd/LTL (1.45)	1.76	7.6	16.0

2.4. Infrared Spectroscopy

The infrared spectra were recorded on a Perkin-Elmer 1720-X Fourier Transform spectrometer at a spectral resolution of 4 cm^{-1} . The catalysts were pressed in a thin self-supporting wafer and placed in an in-situ transmission infrared cell. The catalysts were reduced at 300°C , evacuated at 150°C and then cooled down to room temperature under vacuum. The cell was filled with water saturated helium and allowed to stand overnight. CO was flushed for 2 minutes, after which the CO absorbance spectrum was collected. The spectra were collected under wet conditions to prevent ion-dipole interaction between potassium and the adsorbed CO^[21]. The spectra were corrected for the absorption of the zeolite and gas phase CO.

3. RESULTS

3.1. Catalytic reactions

Analysis of the reaction products for neopentane conversions between 0.5 to 5.0% by the Delplot method^[22] indicates that the primary reaction products are methane, isobutane (hydrogenolysis) and isopentane (isomerisation). The selectivities are given in Table 2. At 325°C , methane and isobutane are produced in nearly equimolar amounts for Pd/LTL(0.55) and Pd/LTL(1.01), but the ratio increases with increasing reaction temperature. This indicates that multiple hydrogenolysis becomes significant at the higher temperatures. Furthermore, the hydrogenolysis selectivity decreases with increasing alkalinity of the support.

The Turnover Frequencies (TOF) for both neopentane and propane conversion are given in Table 3. The TOF's increase continuously as the support acidity increases from alkaline through neutral to acidic supports. For neopentane, the TOF for Pd/LTL(0.55) is 45 times greater than for Pd/LTL(1.01), which is, in turn, 160 times higher than for Pd/LTL(1.45). Similarly, the propane TOF for Pd/LTL(0.55) is approximately 30 times greater than for Pd/LTL(1.01), which is 60 times higher than for Pd/LTL(1.45).

Table 2
Selectivity of neopentane hydrogenolysis¹

Catalyst (K/Al)	Reaction Temperature ($^\circ\text{C}$)	Product selectivity ² , Wt%		
		CH ₄	i-C ₄ H ₁₀	i-C ₅ H ₁₂
Pd/LTL(0.55)	325	19.0	64.8	16.2
	350	26.2	73.8	--
Pd/LTL(1.01)	325	11.0	40.2	48.8
	350	24.4	46.0	29.6
	450	48.6	51.4	--
Pd/LTL(1.45)	450	22.1	40.7	37.2

¹ Atmospheric pressure and 1.25 vol% neopentane in H₂.

² Selectivity determined at 0.5% neopentane conversion.

Table 3
Neopentane¹ and propane² hydrogenolysis Turnover Frequencies

Catalyst (K/Al)	Neopentane TOF (molecules/sec.surface Pd atom)	Propane TOF (molecules/sec.surface Pd atom)
Pd/LTL(0.55)	$5.7 \cdot 10^{-3}$	$2.4 \cdot 10^0$
Pd/LTL(1.01)	$1.3 \cdot 10^{-4}$	$7.5 \cdot 10^{-2}$
Pd/LTL(1.45) ³	$8.1 \cdot 10^{-7}$	$1.2 \cdot 10^{-3}$

¹ Determined at 325°C, atmospheric pressure and 1.25 vol% neopentane in H₂.

² Determined at 400°C, atmospheric pressure and 3.78 vol% propane in H₂.

³ TOF determined at 450°C, and extrapolated to 325°C (neopentane) or 400°C (propane).

While the low activity of Pd/LTL(1.45) could be attributed to blockage of the zeolite pores by excess alkali, the fact that propane, which has a kinetically smaller diameter than neopentane, showed similar decreases in TOF as neopentane suggests that this is not the case. In addition, at the high reaction temperatures propane was converted to propylene at similar rates over all the catalysts, indicating that the palladium particles were exposed to propane in Pd/LTL(1.45) (the propylene conversion was not included in the propane TOF).

3.2. XPS

The XP spectra in Figure 1 indicate that there is a continuous shift in binding energies of both the Pd-3d_{3/2} and the Pd-3d_{5/2} line throughout the Pd/LTL series. The binding energy of Pd/LTL(1.01) (neutral support) in our study is identical to that of palladium metal. The palladium particles appear to be electron deficient in Pd/LTL(0.55) (+0.6 eV) and electron rich in Pd/LTL(1.45) (-0.8 eV) compared to palladium on the neutral support (Table 4). The Si 2p, Al 2p, O1s peaks of the supports have the same binding energy, full-width-half-maximum, and intensity ratio's throughout the series and are identical to the data of the bare zeolite.

Table 4
XPS binding energies of Pd/LTL(x.xx)

Catalyst (K/Al)	Binding energy (± 0.1 eV)	
	Pd 3d _{3/2}	Pd 3d _{5/2}
Pd/LTL(0.55)	340.8	335.5
Pd/LTL(1.01)	340.2	334.9
Pd/LTL(1.45)	339.5	334.1

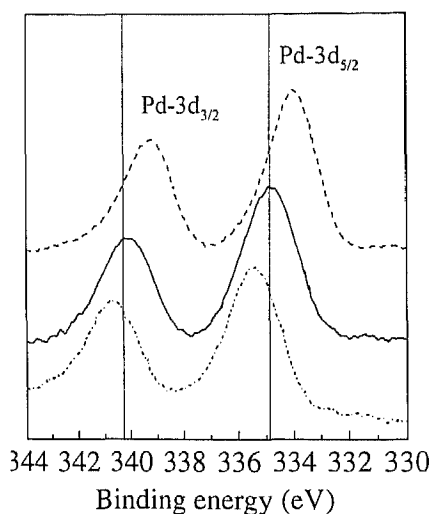


Figure 1. Binding energy of Pd-3d_{5/2} and Pd-3d_{3/2} lines. Dotted line: Pd/LTL(0.55). Solid line: Pd/LTL(1.01). Dashed line: Pd/LTL(1.45). Vertical lines indicate binding energies for Pd-metal.

3.3. Infrared spectroscopy

In the infrared spectra (Figure 2) two kinds of adsorbed CO can be assigned: at higher wavenumbers an absorption band due to linearly coordinated CO, and at lower wavenumbers an absorption band of CO in bridged coordination. For both the linear- and bridged-CO absorption a shift is observed towards lower wavenumber in the series from Pd/LTL(0.55) to Pd/LTL(1.45). Also the integrated intensity ratio of linear/bridged CO is changed (Table 5).

Both observations indicate that the metal particles become more electron rich in the series Pd/LTL(0.55), Pd/LTL(1.01) to Pd/LTL(1.45). A higher electron density on the particles results in more π -backdonation from the metal to CO, which lowers the C-O bond strength, resulting in a shift towards lower wavenumber. Moreover, CO prefers the bridged sites over the linear sites when the metal is capable of donating more electrons into the $2\pi^*$ -orbital of CO^[23], consistent with increasing metal electron density of palladium with increasing support alkalinity.

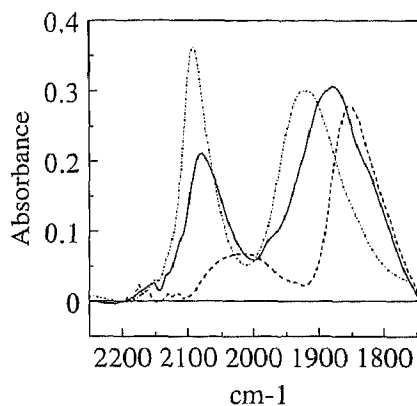


Figure 2. Infrared spectra of CO adsorbed on Pd/LTL(x.xx). Dotted line: Pd/LTL(0.55). Solid line: Pd/LTL(1.01). Dashed line: Pd/LTL(1.45).

4. DISCUSSION

Previous studies of Pd/Y zeolite indicated that Pd on acidic supports has a higher binding energy compared to bulk palladium and Pd on neutral supports^[13-14]. Also, in this study, the XPS binding energy of acidic Pd/LTL(0.55) is higher than for the neutral Pd/LTL(1.01), which is similar to that of bulk palladium. A new observation is that the binding energy continued to decrease to below the value for bulk Pd, as the support is changed from neutral to alkaline.

Table 5
IR data of CO adsorbed on Pd/LTL(x.xx)

Catalyst (K/Al)	Peak maxima (cm ⁻¹)		Integrated intensity ratio linear/bridged CO
	linear CO	bridged CO	
Pd/LTL(0.55)	2091	1920	0.57
Pd/LTL(1.01)	2080	1877	0.39
Pd/LTL(1.45)	2018	1853	0.32

In XPS, the binding energy has been shown to be particle size dependent, increasing by ca. 0.5eV as the particle size is decreased from 50 to 10 Å^[24]. However, TEM and EXAFS of the catalysts in the current study indicate that the particle sizes of the catalysts are almost the same, with all particles less than 15 Å. Therefore, the change of 1.5 eV in binding energies (from acidic to alkaline) is much larger than can be accounted for by the small differences in particle size among these catalysts. Since the shifts in binding energy are not due to particle size effects, they are most probably the result of an interaction of the metal with the support, which causes the binding energies to change continuously as the support is changed from acidic to neutral to alkaline. The palladium particles can be either electron deficient (on acidic supports) or electron rich (on alkaline supports) compared to bulk palladium.

Additional evidence for a change in electronic properties of the palladium particles in the catalysts is obtained from infrared spectroscopy. Typically, on noble metals, CO bonds in linear and bridged coordination, with the C-O stretching frequency in the spectral regions 2100-2000 cm⁻¹ and 1950-1800 cm⁻¹, respectively. The exact peak position depends on parameters as particle size, surface coverage and electronic changes in the metal structure.

With the Pd particle size and CO coverage the same for the catalyst samples, the frequency shifts observed should be due to a higher backdonation from the metal to CO as a result of changes in electronic properties of the Pd. Also, the relative amounts of linear and bridged CO configurations is influenced by variations in the electronic properties of the metal, like work-function and d-band occupancy^[23,25]. With a higher d-band occupation, CO in bridge coordination is favoured over CO in linear coordination. The decrease in linear/bridge ratio together with a shift to lower wavenumbers, observed with infrared spectroscopy, throughout the series from Pd/LTL(0.55) to Pd/LTL(1.45) is therefore in agreement with the Pd-3d binding energy shift observed with XPS.

As previously observed for hydrogenolysis of neopentane^[1,5-7], and propane^[4,5], the hydrogenolysis TOF is higher for palladium on acidic supports as compared to neutral supports. Furthermore, the TOF is observed to decrease further as the support becomes alkaline, consistent with results reported for Pt/LTL^[5]. In addition, selectivity towards hydrogenolysis also decreases with decreasing support acidity, which is also consistent with results reported for Pt/LTL. Thus, the changes in catalytic properties are not limited to differences between acidic and neutral supports, but decrease continuously as the support is changed from acidic to neutral to alkaline.

TOF's for both propane and neopentane conversion seem to be closely correlated with the XPS binding energy (Figure 3). The fact that ln(TOF) for both reactants, measured under different conditions, are both linearly related to the binding energy indicates that the metal-support interactions which induce the change in binding energy can also be responsible for the change in catalytic properties.

While for acidic and neutral supports similar changes in catalytic and spectroscopic properties have been previously reported, the results of this study show that these effects also extend to alkaline supports. These gradual changes can be related to the metal-support interaction, that depends on the acidity or alkalinity of the support.

Previously, the high specific activity for neopentane hydrogenolysis for the electron deficient palladium was ascribed to the formation of metal-proton adducts, in which the charge from the proton is delocalised over the palladium particles [6-7,14,18]. However, the continuous shift in catalytic and spectroscopic properties of the metal as the support becomes alkaline, where acidic hydroxyls are not present, indicates that the change in metal properties is probably not due only to an interaction with acidic hydroxyls.

Models which describe this metal-support interaction only in terms of the support acidic properties seem incomplete since they cannot account for the changes in the metal properties with the alkaline supports. We suggest that the interaction is either due to interaction with the support oxygen atoms, the cations in the zeolite, or both. However, the details of this metal-support interaction are not yet understood, and will be subject of future investigations.

5. CONCLUSIONS

A continuous change in catalytic and spectroscopic properties of small palladium clusters is observed as the support is varied from acidic to neutral to alkaline. The changes in these properties are due to an electronic modification of the small palladium clusters caused by the modification of the support.

ACKNOWLEDGEMENT

The authors would like to thank Prof. J.W. Geus (Utrecht University) for the transmission electron micrographs.

REFERENCES

1. Dalla Betta, R.A., Boudart, M., Proc. 5th Int. Cong. on Catal., (J.W. Hightower, ed.), North Holland Pub. Co., **2** (1973) 1329
2. Figueras, F., Gomez, R., Primet, M., Adv. Chem. Ser., No. 121 (1973) 480
3. Lin, S.D., Vannice, M.A., J. Catal., **143** (1993) 539
4. Vaarkamp, M., Miller, J.T., Modica, F.S., Lane, G.S., Koningsberger, D.C., Proc. 10th Int. Cong. on Catal., Budapest (1992) 809

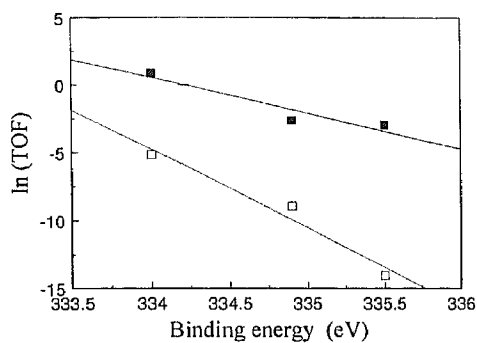


Figure 3. Correlation between Pd-3d_{3/2} binding energy and ln(TOF) for neopentane (open squares) and propane (closed squares) hydrogenolysis.

5. Miller J.T., Modica, F.S., Meyers, B.L., Koningsberger, D.C., *Prep. ACS Div. Petr. Chem.*, **38** (1993) 825
6. Karpinski, Z., Gandhi, S.N., Sachtler, W.M.H., *J. Catal.*, **141** (1993) 337
7. Homeyer, S.T., Karpinski, Z., Sachtler, W.M.H., *J. Catal.*, **123** (1990) 60
8. Gallezot, P., Datka, J., Massardier, J., Primet, M., Imelik, B., *Proc. 6th Int. Cong. Catal. (G.C. Bond, P.B. Wells, F.C. Tompkins, eds.)* **2** (1977) 696
9. Naccache, C., Primet, M., Mathieu, M.V., *Adv. Chem. Ser.*, **121** (1973) 66
10. Vendrine, J.C., Dufaux, M., Naccache, C., Imelik, B., *J. Chem. Soc. Farad. Trans. I*, **74** (1978) 440
11. Foger, K., Anderson, J.R., *J. Catal.*, **54** (1978) 318
12. Ioffe, M.S., Kuznetsov, B.N., Rydin, Y., Yermakov, Y., *Proc. 6th Int. Cong. Catal. (G.C. Bond, P.B. Wells, F.C. Tompkins, eds.)* **1** (1977) 131
13. Stakheev, A.Yu., Sachtler, W.M.H., *J. Chem. Soc. Faraday Trans.*, **87** (1991) 3703
14. Sachtler, W.M.H., Stakheev, A.Yu., *Catal. Today*, **12** (1992) 283
15. Gallezot, P., Weber, R., Dalla Betta, R.A., Boudart, M., *Z. Naturforsch.*, **34a** (1979) 40
16. McHugh, B.J., Larsen G., Haller, G.L., *J. Phys. Chem.*, **94** (1990) 8621
17. Samant, M.G., Boudart, M., *J. Phys. Chem.*, **95** (1991) 4070
18. Tzou, M.S., Sachtler, W.M.H., *Catalysis 1987 (J.H. Ward, ed.) Elsevier Amsterdam* (1988) 233
19. Jansen, A.P.J., Van Santen, R.A., *J. Phys. Chem.*, **94** (1990) 6764
20. Sanchez Marcos, E., Jansen, A.P.J., van Santen, R.A., *Chem. Phys. Lett.*, **167** (1990) 399
21. Kappers, M.J., Vaarkamp, M., Miller, J.T., Modica, F.S., Barr, M.K., van der Maas, J.H., Koningsberger, D.C., *Catal. Lett.*, **21** (1993) 235
22. Bhore, N.A., Klein, M.T., Bischoff, K.B., *Ind. Eng. Chem. Res.*, **29** (1990) 313
23. Van Santen, R.A., *J. Chem. Soc. Faraday Trans. I*, **83** (1987) 1915
24. Nosova, L.V., Stenin, M.V., Nogin, Yu N., Ryndin, Yu A., *Appl. Surf. Sci.*, **55** (1992) 43
25. Van Santen, R.A., *Theoretical Heterogeneous Catalysis*, World Sci. Publ. Co., Singapore (1991) 9