

## The influence of a second metal component (Cu, Sn, Fe) on Pd/SiO<sub>2</sub> activity in the hydrogenation of 2,4-dinitrotoluene

A. Benedetti<sup>1</sup>, G. Fagherazzi<sup>1</sup>, F. Pinna<sup>2</sup>, G. Rampazzo<sup>3</sup>, M. Selva<sup>2</sup>  
and G. Strukul<sup>2</sup>

<sup>1</sup> *Dipartimento di Chimica Fisica*, <sup>2</sup> *Dipartimento di Chimica* and <sup>3</sup> *Dipartimento di Scienze Ambientali; Università di Venezia, Calle Larga St. Marta 2137, Venezia 30123, Italy*

Received 16 January 1991; accepted 25 June 1991

The catalytic activity of palladium in the hydrogenation of 2,4-dinitrotoluene is reduced by the addition of Cu or Sn. Upon addition of Fe, the activity increases. The formation of highly dispersed Pd-Fe bimetallic aggregates is suggested, where the Fe atoms, contiguous to Pd, act as promoters activating of the N=O bond.

**Keywords:** Bimetallic palladium; 2,4-dinitrotoluene hydrogenation; TPR

### 1. Introduction

Supported palladium is one of the most active catalysts in the liquid phase hydrogenation of aromatic nitrocompounds to the corresponding amines [1]. Nevertheless the catalyst undergoes slow deactivation due to sintering of the metal and/or fouling by the by-products formed.

The addition of a second component to a metallic catalyst is a known method for modifying its activity and selectivity. Many papers [2–5] have been published on bimetallic or modified Pd based catalysts for the selective hydrogenation of unsaturated hydrocarbons, but very few results [6] have been reported on the hydrogenation of nitroaromatic compounds.

In this work we report the hydrogenation of 2,4-dinitrotoluene (DNT) to toluenediamine (TDA) on some SiO<sub>2</sub> supported palladium catalysts with different metal loading and dispersions and the effect of a second metal component like copper, tin or iron on the catalyst composition and activity.

## 2. Experimental

Monometallic catalysts were prepared by impregnation of SiO<sub>2</sub> (Akzo Chemie F22; surface area: 400 m<sup>2</sup> g<sup>-1</sup>; particle size range: 100–150 μ) with aqueous solutions of H<sub>2</sub>PdCl<sub>4</sub>. After drying at 110°C, samples were calcined at 500°C for 2 h, then reduced at 250°C for 1 h and passivated (5% O<sub>2</sub> in Ar) before storing in air.

Different batches of the same H<sub>2</sub>PdCl<sub>4</sub>SiO<sub>2</sub> sample, after drying at 110°C, were further impregnated with aqueous solutions of CuCl<sub>2</sub>, SnCl<sub>2</sub> and FeCl<sub>3</sub> in order to obtain the bimetallic catalysts with different M/Pd ratios (M = Cu, Sn, Fe). After drying, samples were calcined, reduced and passivated as described above. The chemical analysis was performed by atomic absorption spectroscopy.

X-ray diffraction (XRD) measurements were carried out in order to perform a line broadening analysis on the available X-ray diffraction peaks to obtain the values of the crystallite size as well as the lattice parameters for the metal phases. Peak profiles were collected using a monochromator on the diffracted beam and a proportional counter with a pulse height discriminator. A CuKα-Ni-filtered radiation and a step-by-step technique were employed (steps of 0.05° with an accumulation counting time of 100 s per angular abscissa).

A best-fit procedure [7], using pseudo-Voigt as analytical functions, was carried out in order to obtain the single profile parameters. The optimized pseudo-Voigt actions relevant to the Kα<sub>1</sub> component were Fourier-transformed and then corrected for the instrumental broadening. A volume-weighted average crystallite size,  $D_v$ , was calculated by a single profile analysis (111 of the Pd or of the PdCu alloyed systems) assigning all the broadening to the crystallite size.

The average palladium particle size in the monometallic catalysts was also measured by H<sub>2</sub> and CO chemisorption using a pulse flow technique. Thermal pretreatment, prior to chemisorption measurements, involved exposure to hydrogen at 250°C for 2 h followed by argon purge at the same temperature for 3 h. The samples were then cooled in inert atmosphere to 25°C for measurement of CO chemisorption and to 70°C for H<sub>2</sub> chemisorption to avoid hydride formation with Pd [8].

Temperature-Programmed Reduction (TPR) measurements were performed in a standard apparatus by the same technique as described by Hurst et al. [9]. The calcined samples (500°C) were heated at a linear rate of 15°C/min from room temperature to 750°C with a gas (5% H<sub>2</sub>/Ar) flow of 40 ml (STP)/min. In the case of the monometallic catalysts, the total amount of Pd in the sample was kept constant by charging different amounts of catalyst.

The hydrogenations of 2,4-dinitrotoluene were carried out in ethanol solution at atmospheric pressure in a 25 ml round-bottomed flask equipped with a hydrogen reservoir (10 lt) and a side-arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (25 ± 0.5°C) was maintained by water circulation in an external jacket connected with a thermostat. Stirring was

Table 1  
Characterization and reaction data of Pd/SiO<sub>2</sub> catalysts

Pd (wt%)	Particle size (Å)			Dispersion (H/Pd)	Activity (mol 2,4 DNT × h <sup>-1</sup> × g <sup>-1</sup> Pd)	T.N. (s <sup>-1</sup> )
	H <sub>2</sub>	CO	WAXS			
2.2	68	76	80	0.16	2.24	0.41
2.0	55	54	55	0.20	2.58	0.38
2.1	31	35	33	0.36	3.11	0.26
3.2	27	26	28	0.41	2.22	0.16
1.1	23	18	20	0.50	2.34	0.14

performed by a teflon-coated bar driven externally by a magnetic stirrer. Absence of diffusional problems was determined by the independence of conversion vs. time plots on the stirring rate in kinetic experiments.

The catalyst (40 mg) was placed in the reactor, which was evacuated and filled with H<sub>2</sub>. Then 10 ml of a H<sub>2</sub> saturated, 0.2 M solution of DNT in ethanol, containing n-decanol (0.05 M) as internal standard, were added through the septum and time was started. All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Separation of the products was performed on a 2 m OV 17 packed column using a flame ionization detector. Quantitative data were obtained from calibration curves of the reactant and products vs. the internal standard.

### 3. Results and discussion

The specific activity of the Pd/SiO<sub>2</sub> catalysts, expressed as Turnover Numbers, as well as the metal particle sizes obtained with H<sub>2</sub> and CO chemisorption and XRD, are reported in table 1. A good agreement among the particle sizes, determined by different techniques, was found.

In all our activity experiments, which were run in excess of hydrogen, zero-order reaction rate constants were obtained from plots of the concentration of 2,4-dinitrotoluene as a function of time for well over 90% conversion. This could indicate that the nitrocompound is strongly adsorbed on Pd surface and the slow step of the reaction can be ascribed to the H<sub>2</sub> activation or the hydrogenation of the adsorbed nitrocompound.

An almost threefold increase of Turnover Number was found in the range of dispersion studied (0.15–0.50). The higher activity observed on large Pd particles goes along with previous results reported in the literature in the hydrogenation of unsaturated hydrocarbons [10–13] but the interpretation of this particle size effect is still a matter of discussion. It was previously observed [12,13] that the hydrogen absorption, with β-hydride formation, increases with the Pd particle

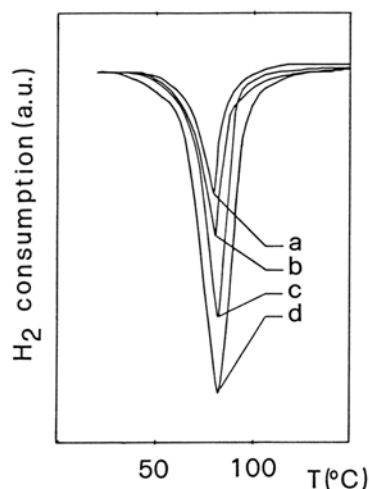


Fig. 1. TPR profiles of Pd/SiO<sub>2</sub> catalysts: (a) Pd(3.2), 28 Å; (b) Pd(2.1), 33 Å; (c) Pd(2.0), 55 Å and (d) Pd(2.2), 80 Å.

sizes. We have obtained some experimental evidence of hydrogen solubility in Pd from the TPR profiles of the monometallic Pd catalysts (fig. 1): since Pd is already reduced below room temperature, in the TPR spectra only a negative peak appeared, centered at  $\approx 80^\circ\text{C}$ , which indicated a hydrogen evolution and was attributed to the Pd- $\beta$  hydride decomposition [14]. The amount of hydrogen evolved from the individual peaks parallels the trend of the corresponding Pd average particle size reported in table 1. Therefore we suggest that the catalytic behaviour of palladium in this reaction can be ascribed to the formation of the  $\beta$ -hydride which would act as a hydrogen reservoir.

If we consider the bimetallic catalysts, a clear influence of the second metal on Pd catalytic activity can be observed (table 2). Since it was not possible to determine the single metal dispersion through chemisorption measurements, the catalytic activity was referred to the Pd total content. The addition of either small amounts of Cu or more significant amounts of Sn strongly reduce the catalytic activity.

Pd and Cu form a continuous series of face-centered-cubic substitutional solid solutions up to a Cu content of about 40 at.% [15]. In these alloys the lattice parameter of the cubic PdCu alloy decreases monotonically with increasing Cu content. Following the results of Burch and Buss [14], the alloy composition was obtained from the unit cell edge of the Pd-Cu catalysts as determined by X-ray diffraction (see table 3).

Table 2  
Activity of modified Pd catalysts

No	Catalyst	Pd particle size (Å) WAXS	Activity (mol 2,4 DNT × h <sup>-1</sup> × g <sup>-1</sup> Pd)
1	Pd(2.2)	80	2.24
2	Pd(2.1)-Cu(0.1)	145	0.36
3	Pd(2.2)-Cu(0.3)	128	0.13
4	Pd(2.2)-Cu(0.5)	133	0.08
5	Pd(2.3)-Sn(1.1)	–	1.63
6	Pd(2.2)-Sn(2.0)	80	0.07
7	Pd(2.0)-Fe(0.8)	100	4.34
8	Pd(2.1)-Fe(1.7)	–	3.93
9	Fe(2.0)	–	0.0

As table 3 clearly shows (samples 3 and 4) copper is present in the alloy. Moreover, the addition of even small amounts of Cu (as in sample 2 for example) increases significantly the metal particle size and the increase seems to be independent of the amount of Cu. On the other hand, this determines a drastic decrease in the catalytic activity. As stated above, an increase in Pd particle sizes should in principle be paralleled by an increase in activity. Since the opposite applies to the present case it seems likely that the alloy formation occurs in all Cu containing catalysts, even in sample 2 where, probably because of the low Cu content, it could not be detected from X-ray diffraction.

In the TPR profiles of the Pd-Cu samples reported in fig. 2, the addition of Cu deeply modified the intensity of the hydrogen evolution peak which was attributed to the Pd-β hydride decomposition: above 0.1% Cu the negative curve disappeared. A major peak at ≈ 190°C, with a lower temperature shoulder, appeared which could be related to the occurrence of the alloy. A small reduction band at ≈ 390°–400°C indicated that some CuO, which had not interacted with Pd, was still present. The existence of a significant amount of free Cu could also explain why the alloy composition obtained from lattice

Table 3  
Lattice parameters and alloy composition in Pd-Cu/SiO<sub>2</sub> samples

No	Catalyst	Lattice parameter <sup>a</sup> <i>a</i> (Å)	Alloy composition (Cu content at.%)
1	Pd(2.2)	3.892 ± 0.005	–
2	Pd(2.1)-Cu(0.1)	3.892 ± 0.004	–
3	Pd(2.2)-Cu(0.3)	3.880 ± 0.002	4.0
4	Pd(2.2)-Cu(0.5)	3.869 ± 0.005	8.5

<sup>a</sup> Computed from the Pd 111, 200, 220 and 311 XRD peaks analysis and from the PdCu alloy 111, 200, 220 XRD peaks analysis (the alloys showed lower peak intensities).

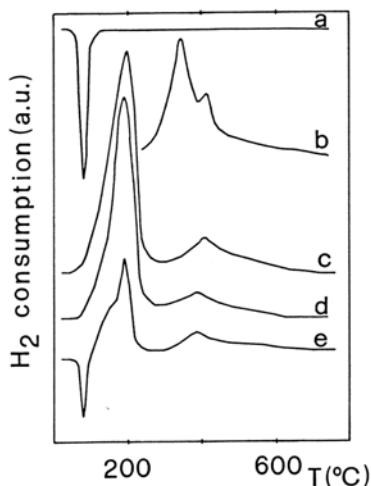


Fig. 2. TPR profiles of (a) Pd(2.2)/SiO<sub>2</sub>; (b) Cu(2.0)/SiO<sub>2</sub>; (c) Pd(2.2)-Cu(0.5)/SiO<sub>2</sub>; (d) Pd(2.2)-Cu(0.3)/SiO<sub>2</sub> and (e) Pd(2.1)-Cu(0.1)/SiO<sub>2</sub>.

parameters resulted lower in Cu content than that computed from weight loading.

As to the disappearance of the negative peak associated to the Pd- $\beta$  hydride formation, this behaviour was already reported in the literature [16–18] upon alloy formation between Pd and Cu. This generally results in a decrease in the hydrogenation activity and therefore, in our case, the observed change of catalytic activity after addition of Cu (table 2) could be associated to a reduction of the amount of activated hydrogen available on the Pd surface, due to the presence of the second metal both in the bulk and on the surface.

As far as the Pd-Sn samples are concerned, broad peaks with very low intensities did not allow the X-ray diffraction analysis of sample 5. Also in the case of sample 6, even if the X-ray pattern showed more defined peaks, we were not able to identify a crystalline single phase in an unambiguous way. No reflections were found below 38° in  $2\theta$  and envelopes of broad superimposed peaks limited our analysis. However the most intense observed peaks of sample 6 ( $2\theta > 38^\circ$ ) were very close to those of a PdSn alloy as reported by Masai et al. [18] for a Pd/Sn = 1 system. The line broadening analysis was carried out on the highest XRD peak also for this sample. Even in this case a drop in catalytic activity is evident (table 2) upon addition of the second metal component, suggesting for the Pd- $\beta$  hydride conclusions similar to the case of Cu. This view is supported by the TPR profiles reported in fig. 3 and by the findings of Figueras et al. [19] on Pd-Sn alloys dispersed on Al<sub>2</sub>O<sub>3</sub>.

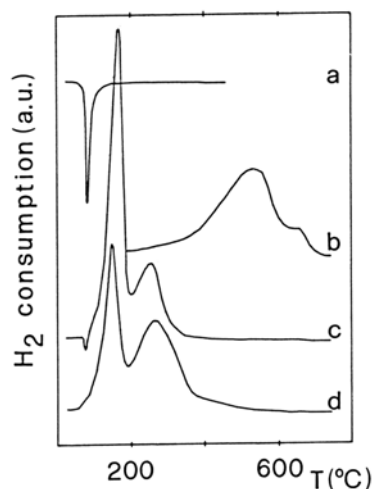


Fig. 3. TPR profiles of (a) Pd(2.2)/SiO<sub>2</sub>; (b) Sn(2.0)/SiO<sub>2</sub>; (c) Pd(2.3)-Sn(1.1)/SiO<sub>2</sub> and (d) Pd(2.2)-Sn(2.0)/SiO<sub>2</sub>.

Unlike Cu and Sn, the addition of Fe increased the catalytic activity of Pd in the hydrogenation of 2,4 DNT, while the Fe/SiO<sub>2</sub> sample resulted to be inactive. The TPR profiles of the two Pd-Fe catalysts together with a Pd/SiO<sub>2</sub> and a Fe/SiO<sub>2</sub> sample are shown in fig. 4. Pure iron reduction profile showed a broad band with two maxima centered at  $\approx 440^\circ$  and  $\approx 590^\circ\text{C}$ , which was attributed [20] to a two-step reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sup>0</sup> through Fe<sub>3</sub>O<sub>4</sub>. As previously shown, in the TPR spectra of pure Pd only a negative peak appeared. With the increase of Fe content, the negative peak became less intense and then disappeared, suggesting that  $\beta$ -hydride phase was inhibited by the addition of Fe. In the profile of the two bimetallic samples, a new sharp peak appeared centered at  $\approx 135^\circ\text{C}$  and a small reduction band of Fe<sub>2</sub>O<sub>3</sub> was still discernible, but shifted at lower temperature. Both findings seem to suggest a strong interaction between Pd and Fe, and still the presence of Fe<sub>2</sub>O<sub>3</sub> which had not interacted with Pd.

The possible formation of an alloy could not be verified unambiguously by X-ray diffraction analysis, because of a drastic decrease of the intensity of the diffraction peaks in sample 7. Moreover, in sample 8, which contains still 2.1% Pd, only the presence of  $\alpha$ -Fe and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> could be evidenced. Clearly, the corresponding Pd particle sizes reported in table 2, refer to the fraction of palladium that is accessible to XRD. Since both Pd-Fe catalysts contain about 2% Pd, these preliminary data seem to suggest the formation of highly dispersed

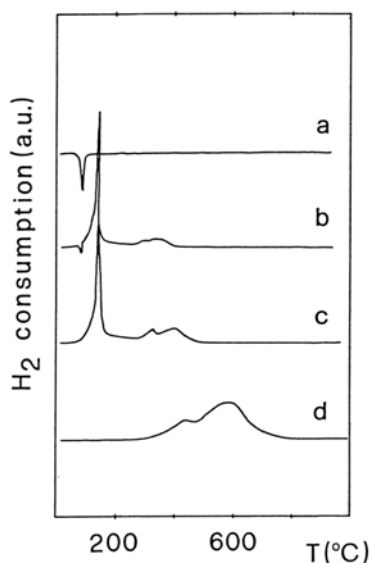


Fig. 4. TPR profiles of (a) Pd(2.2)/SiO<sub>2</sub>; (b) Pd(2.0)-Fe(0.8)/SiO<sub>2</sub>; (c) Pd(2.1)-Fe(1.7)/SiO<sub>2</sub> and (d) Fe(2.0)/SiO<sub>2</sub>. After reaching 750 °C the temperature is maintained constant.

bimetallic aggregates with dimensions below the detection limit of XRD ( $\approx 15$  Å). These aggregates could be responsible for the increased reactivity in the hydrogenation of 2,4-dinitrotoluene through the polarization of the N=O bond, by coordination of the oxygen on Fe atoms contiguous to Pd.

#### Acknowledgment

The financial support from MURST (60%) is gratefully acknowledged.

#### References

- [1] G.C. Bond and P.B. Wells, *Advan. Catal. Relat. Subj.* 15 (1964) 92.
- [2] W.M.H. Sachtler, *Catal. Relat. Rev. Sci. Eng.* 14 (1976) 193.
- [3] V. Ponec, *Advan. Catal. Relat. Subj.* 32 (1983) 143.
- [4] J.P. Boitiaux, J. Csny, M. Derrien and G. Léger, *Hydrocarbon Processing* 3 (1985) 51.
- [5] T. Mallat, J. Petrò, S. Szabò and J. Sztatisz, *React. Kinet. Catal. Lett.* 29 (1985) 353.
- [6] U.S. Patent 2, 823, 235 Du Pont.
- [7] S. Enzo, S. Polizzi and A. Benedetti, *Z. Kristallogr.* 170 (1985) 275.



- [8] C.L.M. Joyal and J.B. Butt, *J. Chem. Soc., Faraday Trans. I*, 83 (1987) 2757.
- [9] N.W. Hurst, S.J. Gentry, A. Jones and B.D. McNicol, *Catal. Relat. Rev. Sci. Eng.* 24 (1982) 233.
- [10] A. Borodzinski, R. Dus, R. Frak, A. Janko and W. Palczewska, in: *Proc. 6th Int. Congr. Catalysis*, eds. G.C. Bond, P.B. Wells and F.C. Tompkins, Vol. 1 (The Chemical Society, London, 1976) p. 150.
- [11] G. Gubitosa, A. Berton, M. Camia and N. Pernicone, in: *Preparation of Catalysts III*, eds. G. Poncelet, P. Grange and P.A. Jacobs (Elsevier Science Publishers, Amsterdam, 1983) p. 431.
- [12] M. Boudart and H.S. Hwang, *J. Catal.* 39 (1975) 44.
- [13] R. Pitchai, S.S. Wong, N. Takahashi, J.B. Butt, R.L. Burwell Jr. and J.B. Cohen, *J. Catal.* 94 (1985) 478.
- [14] J. Lietz, M. Nimz and J. Volter, *Appl. Catal.* 45 (1988) 71.
- [15] R. Burch and R. G. Buss, 3. C. S. *Faraday Trans. I*, 71 (1975) 913.
- [16] T. Mallát and J. Petrò, *Acta Chim. Hung.* 112 (1983) 173.
- [17] S. Leviness, V. Nair, A.H. Weiss, Z. Schay and L. Guszi, *J. Mol. Catal.* 25 (1984) 131.
- [18] M. Masai, K. Honda, A. Kubota, S. Ohnaka, Y. Nishikawa, K. Nakahara, K. Kishi and S. Ikeda, *J. Catal.* 50 (1977) 419.
- [19] H.R. Aduriz, P. Bodnariuk, B. Coq and F. Figueras, *J. Catal.* 119 (1989) 97.
- [20] E.E. Unmuth, L.H. Schwartz and J.B. Butt, *J. Catal.* 87 (1983) 8.

