

CS₂ poisoning of size-selective cubooctahedral Pd particles in styrene hydrogenation

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The poisoning effect of carbon disulfide on cubooctahedral palladium nanoparticles (1.5, 3.0 or 4.6 nm in mean diameter) deposited on montmorillonite was investigated in the liquid-phase hydrogenation of styrene to ethylbenzene under mild conditions. The dispersion of the metal crystallites was computed as a function of the mean diameter in terms of face atoms, of edge atoms + corner atoms, and of the total number of exposed surface atoms. A linear relationship was found between the rate of hydrogenation and the fraction of low-coordination surface sites poisoned, independently of particle size, and hydrogenation ceased when these sites were quantitatively covered by poison molecules with a nominal stoichiometry of CS₂:Pd = 1:2. High-coordination terrace sites are not involved in the hydrogenation reaction.

KEY WORDS: hydrogenation; palladium; nanoparticles; montmorillonite; carbon disulfide; poisoning; styrene.

The number of exposed metal atoms at the solid/gas interface, determined in chemisorption experiments, may differ significantly from the number of catalytically active surface sites observed at the solid/solution interface under reaction conditions. For traditional supported metal catalysts applied in liquid-phase hydrogenations, quantitative CS₂ poisoning provides a good alternative for a better estimate of the percentage of active metal sites: the number of active sites determined by CS₂ titration was found to be a fraction of that determined by CO and H₂ chemisorption [1–4]. A fundamental study of nanocluster catalyst poisoning and a review of the related literature have been reported by Hornstein *et al.* [4], who paid particular attention to the relationship between the specific rate of hydrogenation of the olefinic bond and the number of surface sites poisoned. This challenging work inspired us to carry out a systematic study on the CS₂ poisoning of a series of supported metal catalysts differing in the size of the metal particles, but not in other respects.

We recently developed a controlled colloid synthesis method which provides a series of low-loaded Pd/montmorillonite (Pd-M) catalysts (0.15 wt% each) containing fairly monodisperse Pd particles with cubooctahedral morphology [5,6]. The mean diameter of the particles, and hence the relative concentrations of high-coordination face atoms (terrace sites) and low-coordi-

nation edge and corner atoms (defect sites), was systematically altered from 1.5 to 6.2 nm with the aim of finding a correlation between the catalytic activity and the numbers of surface sites of these kinds. The liquid-phase hydrogenation of styrene to ethylbenzene under mild conditions is ideally suited for this catalytic probe, because the reaction follows zero-order kinetics with respect to styrene throughout the entire range of conversion [5,7]. Consequently, the occurrence of gradual activation or deactivation of the catalyst during the reaction can be excluded. The good correlation between the turnover frequencies (TOFs) on a per-active-metal-atom basis and the defect site densities of the Pd cubooctahedra led us to conclude that hydrogenation occurs on these defect sites and that terrace sites are not involved in the reaction. Here, we additionally report on a CS₂ poisoning study which leads to similar conclusions.

Figure 1 depicts the dispersion of the cubooctahedral Pd particles as a function of the mean diameter computed for the terrace sites (face atoms only) or the defect sites (edge + corner atoms) and the total number of (terrace + defect) surface sites [5]. The symbols in figure 1 at 1.5, 3.0 and 4.6 nm represent the dispersions of Pd-M15, Pd-M30 and Pd-M46, respectively, selected for use in the present poisoning study. The preparation and characterization of these catalysts were described earlier [5]. For the design of a set of experiments, we assumed that the active ensemble of surface sites is composed only of edge and corner atoms and that these sites will be poisoned first by CS₂ molecules. With the

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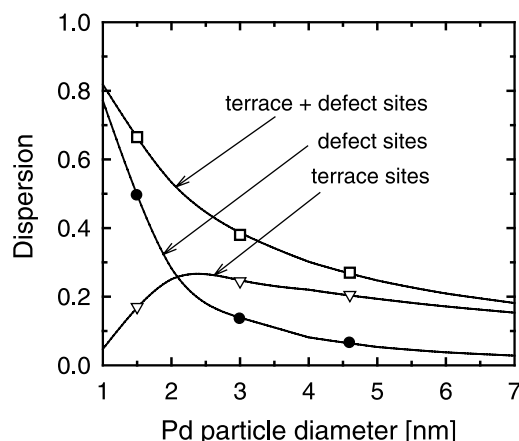


Figure 1. Dispersion of cubooctahedral Pd particles, calculated for terrace sites (face atoms only), defect sites (edge + corner atoms) and the total number of exposed surface sites [5]. The apparent metal dispersions for the catalysts Pd-M15, Pd-M30 and Pd-M46 are indicated by the symbols at 1.5, 3.0 and 4.6 nm, respectively.

further assumption of a stoichiometry of CS₂:Pd = 1:2 [1,4], the theoretical amount of CS₂ required to poison a given fraction of active sites was calculated from the dispersion data in figure 1 (solid symbols). Correction for unexposed Pd atoms in contact with the underlying support was made on a statistical basis [5]. The automated slurry reactor used in the present hydrogenation/poisoning study has been described elsewhere [8]. The catalyst (of the order of 30 mg) was weighed in the reaction vessel and treated in a hydrogen atmosphere, both before and after the addition of 1 mL THF as reaction medium. Next, a known amount of freshly made CS₂ solution (8×10^{-5} M in THF) was injected into the suspension. The substrate was then introduced to give a (total) Pd:styrene molar ratio of 1:2000. The reaction was left to proceed under vigorous stirring at 298 K at a H₂ pressure of 230 kPa. The consumption of H₂ was monitored continuously during the reaction. The above procedure was repeated with increasing amounts of CS₂ until the hydrogenation ceased. Fresh catalyst samples were used in each run. Blank experiments indicated that the extent of adsorption of CS₂ on the support material was negligible: the rate did not change when additional support material, free of Pd, was present in the reaction system. A full set of experimental results for Pd-M30 is depicted in figure 2. The kinetic curves are linear over a large range of conversion, which corresponds to zero-order kinetics [5,7]. The reaction rates were calculated from the slopes of the straight lines and were then normalized with respect to the rate measured on the non-poisoned catalyst. The relative rate of reaction defined in this way gradually decreased from 1 to 0 as the fraction of active sites poisoned progressively increased from 0 to 1. For the three Pd-M catalysts studied, the relative rates of reaction at different levels of poisoning are plotted in figure 3.

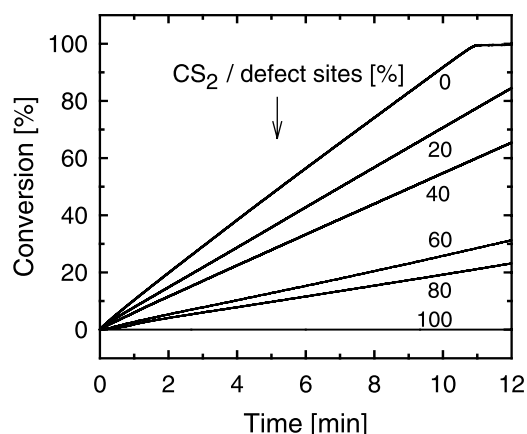


Figure 2. A series of kinetic curves for the conversion of styrene to ethylbenzene on Pd-M30. The percentage of defect sites deactivated by CS₂ is indicated for each curve. (Solvent: THF; $T = 298.15$ K; $p = 230$ kPa H₂; styrene : Pd = 2000.)

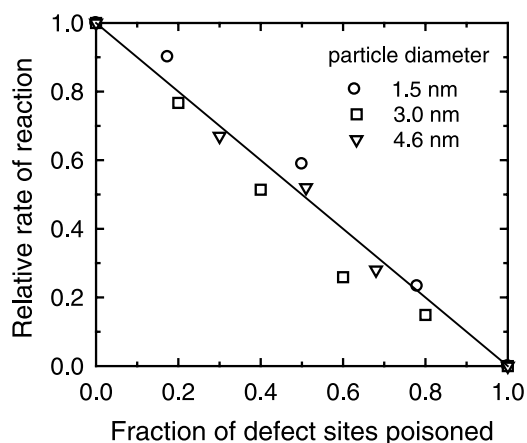


Figure 3. Rates of hydrogenation of styrene to ethylbenzene on Pd-M15, Pd-M30 and Pd-M46, relative to the rate on the non-poisoned catalyst, at various fractions of active sites poisoned.

The diagonal is the theoretical line when one CS₂ molecule occupies two Pd atoms on the ensemble of low-coordination surface sites. The experimental data are close to this straight line. The scatter around the diagonal is within experimental error, which mainly originates from unresolved surface imperfections. Although TEM and HRTEM micrographs revealed that the Pd particles are fairly uniform cubooctahedral nanocrystallites [5,6], the particles are not strictly monodisperse and it is unlikely that they are perfect crystallites; different kinds of edge atoms, corner atoms, terrace vacancies and adatoms, all differing in degree of coordination unsaturation, may therefore be exposed to the surface. In spite of these uncertainties, we may conclude that (i) the results of the present quantitative poisoning study are consistent with the cubooctahedral shape of the catalyst particles; (ii) the hydrogenation of styrene to ethylbenzene occurs on low-coordination

edge and corner atoms; (iii) high coordination face atoms are not involved in this reaction; (iv) the hydrogenation follows zero-order kinetics with respect to the substrate; (v) the adsorption of CS₂ on defect sites is strongly preferred to its adsorption on terrace sites; (vi) the chemisorption of CS₂ on the active sites complies with the stoichiometry CS₂:Pd = 1:2; (vii) the rate of hydrogenation decreases linearly with, and in proportion to, the fraction of defect sites poisoned; (viii) the nominal value of the per-active-metal-atom TOF in THF at 298 K and 230 kPa H₂ is $30.6 \pm 1.9 \text{ s}^{-1}$ (as compared with $41.2 \pm 1.7 \text{ s}^{-1}$ in toluene [5]); (ix) this value appears to be independent of the particle size and the extent of poisoning unless all the active sites are blocked. The size effects of a series of well-defined homopolymer stabilized Pd colloids have recently been investigated with regard to the catalytic Heck reactions [9] and Suzuki reactions [10]. The present study clearly confirms the advantages of applying smart systems in fundamental studies on supported metal catalysis.

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References

- [1] L. Gonzalez-Tejuca, K. Aika, S. Namba and J. Turkevich, *J. Phys. Chem.* 81 (1977) 1399.
- [2] S.-Y. Chen, B. J. McCoy and J. M. Smith, *AIChE J.* 32 (1986) 2056.
- [3] F. Notheisz, Á. Zsigmond, M. Bartók, Zs. Szegletes and G.V. Smith, *Appl. Catal. A: Gen.* 120 (1994) 105.
- [4] B. J. Hornstein, J. D. Aiken III and R. G. Finke, *Inorg. Chem.* 41 (2002) 1625.
- [5] B. Veisz, Z. Király, L. Tóth and B. Pécz, *Chem. Mater.* 14 (2002) 2882.
- [6] B. Veisz and Z. Király, *Langmuir* 19 (2003) 4817.
- [7] G. Carturan, G. Facchin, G. Cocco, S. Enzo and G. Navazio, *J. Catal.* 76 (1982) 405.
- [8] Á. Mastalir and Z. Király, *J. Catal.* 220 (2003) 372.
- [9] J. Le Bars, U. Specht, J. S. Bradley and D. G. Blackmond, *Langmuir* 15 (1999) 7621.
- [10] Y. Li, E. Boone and M. A. El-Sayed, *Langmuir* 18 (2002) 4921.