Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 245 (2007) 267–271
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Liquid chromatography as a novel method for determination of the dispersion of supported Pd particles

Zoltán Király [a,*], Ágnes Mastalir [b,*], Ágota Császár [b], Hilal Demir [c], Deniz Uner [c], Gerhard H. Findenegg [d]

[a] *Department of Colloid Chemistry, University of Szeged, Aradi Vt. 1, H-6720 Szeged, Hungary*
[b] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, H-6720 Szeged, Hungary*
[c] *Department of Chemical Engineering, Middle East Technical University, TR-06531 Ankara, Turkey*
[d] *Stranski-Laboratory for Physical and Theoretical Chemistry, Technical University of Berlin, Strasse des 17. Juni 112, D-10623 Berlin, Germany*

Received 4 August 2006; revised 11 October 2006; accepted 16 October 2006

Abstract

A solution-based method has been developed for determination of the number of active centers on Pd particles responsible for alkene hydrogenation in the liquid phase. Pd/γ-Al_2O_3 was placed in a liquid chromatographic (LC) column, and the CS_2 uptake of the catalyst was determined by applying CS_2 pulses in methanol solution until surface saturation was attained. The reliability of the LC method was confirmed by quantitative CS_2 poisoning of the catalyst in the liquid-phase hydrogenation of styrene to ethylbenzene in methanol solution to give 5.5 ± 0.3 mol CS_2 per 100 mol of total Pd. With the adsorption stoichiometries of Pd/CO = 1 and Pd/H = 1, CO and H_2 adsorption calorimetry furnished $D_G = 36\%$ for the gas-phase dispersion of the metal. This value is close to the $D_{TEM} = 33\%$ obtained from transmission electron microscopy analysis. With the assumption of $Pd/CS_2 = 6$, gas-phase and liquid-phase dispersion measurements provide mutually consistent results; in this case, the liquid-phase dispersion of the metal is $D_L = 33\%$. However, with the more generally accepted stoichiometry of $Pd/CS_2 = 2$, solution-phase experiments yield $D_L = 11\%$. This result implies that the number of exposed metal atoms determined from chemisorption experiments at the solid–gas interface is not equivalent to the number of catalytically active surface sites at the solid–liquid interface.

1. Introduction

Supported Pd catalysts are widely used in liquid-phase hydrogenations for many important organic transformations [1]. Knowledge of the dispersion D of the metal particles is critically important for characterizing catalyst activity in terms of turnover frequency (TOF). On a per active metal atom basis, $TOF = R/D$, where R is the (initial) rate of the reaction and D is the number of active surface atoms relative to the total number of metal atoms [2–4]. Gas chemisorption measurements of CO, H_2, and O_2 on supported Pd catalysts are often used to determine the number of exposed metal atoms, with the assumption of a certain generally accepted stoichiometry for the metal/adsorbate site [2,5–7]. However, there is no a priori reason to believe that the percentage of exposed metal atoms at the solid–gas interface determined in chemisorption experiments is equal to the percentage of catalytically active surface sites at the solid–solution interface under given reaction conditions. For supported metal catalysts applied in liquid-phase hydrogenations, quantitative CS_2 poisoning provides a good alternative for a better estimate of the percentage of active metal sites. In fact, the number of active sites determined by CS_2 titration has often been found to be a fraction of that determined by CO and H_2 chemisorption [4,8–12]. Although attempts have been made to measure gas adsorption into liquid dispersions [13], a rapid and reliable solution-based standard method for determining the number of catalytically active sites remains unavailable.

In the present study, we propose an efficient and simple method, liquid chromatography (LC), for determining the dispersion of supported Pd nanoparticles at the solid–solution in-

---

[*] Corresponding authors.
E-mail addresses: zkiraly@chem.u-szeged.hu (Z. Király), mastalir@chem.u-szeged.hu (Á. Mastalir).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.10.016

terface. The active sites of a commercial Pd/γ-Al_2O_3 catalyst in a LC column were successively saturated with CS_2 pulses in a stream of methanol. The CS_2 uptake determined by the LC method was cross-checked by quantitative CS_2 poisoning of the catalyst in the hydrogenation of styrene to ethylbenzene in methanol in a series of kinetic experiments, until hydrogenation ceased. For further comparison, the chemisorption capacities of CO and H_2 on the catalyst were determined by gas-phase adsorption calorimetry under standard conditions. Liquid-phase dispersion (D_L) and gas-phase dispersion (D_G) data were calculated from generally accepted metal-to-adsorbate stoichiometry ratios, and the results were compared and interpreted.

2. Experimental

2.1. Materials

Pd/γ-Al_2O_3 (5 wt% Pd) was purchased from Merck-Schuchardt (lot no. S24098948). Methanol and CS_2 (HPLC grade, >99.9%) were Aldrich chemicals and used as received. Styrene (99%, Aldrich) was distilled under reduced pressure before use. H_2 and CO (quoted purity >99.99%) were obtained from Oksan. Further purification was conducted by passing the gases through moisture absorbers and activated carbon filters.

2.2. Methods

2.2.1. BET surface area determination

Measurements were made using a Gemini 2375 (Micromeritics) gas sorption apparatus. The Pd/γ-Al_2O_3 catalyst had a N_2 BET surface area of 192 m^2/g at 77 K.

2.2.2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The Pd content of the catalyst was determined by ICP-AES (Jobin Yvon 24) to be $4.9 \pm 0.3\%$ by weight. Before analysis, the sample was dissolved in a 1:2 mixture of aqua regia and 0.5 M $(NH_4)HF_2$. The Pd concentration was obtained from the emission intensities at 229.7 and 324.3 nm by means of calibration curves.

2.2.3. Gas-phase adsorption microcalorimetry

The amounts of H_2 and CO adsorbed and the associated heat effects were measured at 323 K using a Setaram C-80 Tian-Calvet twin-port calorimeter coupled to a multiport high-vacuum Pyrex glass manifold. The manifold was supplied with a Baratron capacitance manometer (Varian CeramiCel) capable of monitoring pressure in the range of 1.3×10^{-5} to 1.3 kPa. The schematics of the adsorption apparatus and the peripherals have been reported previously [15,16]. A 0.5-g catalyst sample was reduced in situ in H_2 at 423 K for 4 h. Higher-temperature treatment of the high-loaded catalyst might have caused sintering of the Pd particles. After the reduction process, the sample was evacuated for approximately 10 h while the catalyst bed cooled down to 323 K. Measurements of the differential heats of H_2 adsorption were conducted at this temperature to minimize the effects of β-hydride formation at lower temperatures. For internal consistency, CO adsorption measurements were conducted under the same conditions as for H_2 by introducing small doses of gas onto the samples. The resulting heat response for each dose was recorded as a function of time and integrated to determine the energy released. The amount of gas adsorbed was determined volumetrically from the dose and equilibrium pressures.

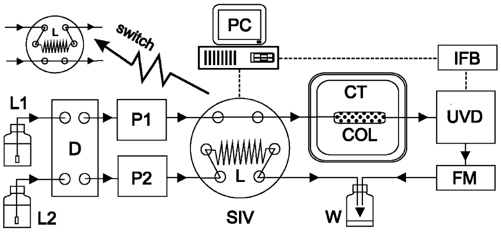

Fig. 1. Experimental setup of LC applied for the measurement of the liquid-phase dispersion of a 5 wt% Pd/γ-Al_2O_3 catalyst by the injection of CS_2 pulses in a stream of methanol. L1, eluent reservoir (methanol); L2, CS_2 solution (4 mM in methanol); D, on-line solvent degasser; P1 and P2, HPLC pumps; SIV, electric sample injection valve; L, sample loop; PC, personal computer; IFB, interface box; COL, adsorption column loaded with the catalyst; CT, column thermostat; UVD, UV detector; FM, flow meter; W, waste container.

2.2.4. Liquid chromatography

Here we describe a novel instrumental technique applied for the first time to determine the dispersion of supported Pd catalysts in the liquid phase. This technique is an improved version of the LC method designed for studying the high-affinity adsorption of surfactants at solid–solution interfaces [17,18]. Various parts and accessories were integrated into a Knauer high-performance liquid chromatograph (HPLC) system; the experimental setup is outlined in Fig. 1. The stainless steal adsorption vessel (column length, 25 mm; i.d., 3.5 mm) was loaded with ca 0.2 g of Pd/γ-Al_2O_3 and placed inside a column thermostat (Smartline 4000) at 298.15 ± 0.1 K. The column was flushed overnight with a reductive solvent (pure methanol) at a constant flow rate of about 10 ml/h using an HPLC pump (WellChrom K-1001). In parallel, 4 mM CS_2 in methanol was percolated through the sample loop (100 µl) of a PC-controlled injection valve (WellChrom K-6) using another HPLC pump operated at the same flow rate as the first pump. Efficient degassing to <0.5 ppm O_2 was achieved using a Smartline Manager low dead-volume (480 µl) two-channel on-line solvent degasser. After equilibration, the CS_2 solution percolated through the sample loop was introduced into the column by the electric switching valve (Fig. 1, insert). Uniform aliquots of the CS_2 solution were injected onto the catalyst bed in a series of small pulses, with evenly distributed time intervals sufficient for attaining thermal equilibrium between them. In this way, the active surface sites were saturated in a successive manner. The concentration profile passing through the column was continuously monitored at a wavelength of 317 nm by a UV detector (WellChrom K-2600) connected to the exit port of the column. For each injection, the amount of CS_2 adsorbed was calculated as the difference in UV peak area between the input pulse and the output pulse. The magnitude of the input pulse was conveniently measured in a separate blank experiment in the absence of the catalyst (reference peak). Correction was made for the

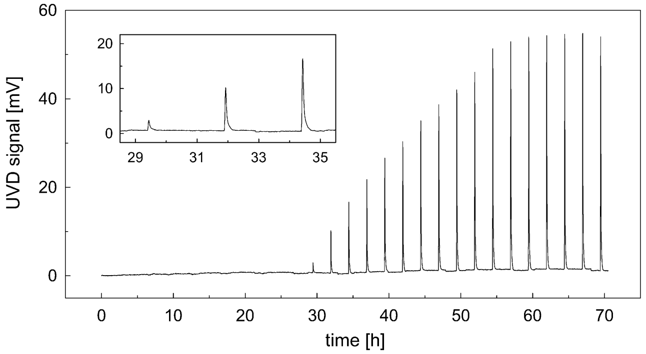

Fig. 2. UV-detector signal of the incremental chemisorption of CS_2 from methanol solution onto Pd/γ-Al_2O_3, as determined by liquid chromatography at 298.15 K (mass of catalyst, 188.4 mg; flow rate, 110 µl/min; pulse volume, 100 µl; CS_2 concentration, 3.82 mM; wavelength, 317 nm).

loss of volatile CS_2 on degassing (4.3%), which was determined via a calibration curve constructed in the absence of the degasser. Fig. 2 shows the response curves of the UVD signal (concentration profile) for a series of injections. Initially, at low surface coverage, no UVD peaks were detected because of the nonreversible nature of the adsorption of CS_2 by the Pd particles. Afterwards, however, the output UVD peaks gradually increased until a steady value was reached as the adsorption leveled off.

It should be emphasized that for a clean surface, the application of both an efficient solvent degasser and a reductive solvent as an eluent liquid were important conditions for catalyst pretreatment. For safety precautions, attention must be paid to the opening of the adsorption vessel, because methanol-treated Pd/γ-Al_2O_3 exposed to air is a strongly pyrophoric material.

2.2.5. *Quantitative catalyst poisoning*

The PC-interfaced three-phase slurry reactor used in the hydrogenation/poisoning experiments has been described elsewhere [19,20]. A 10-mg sample of the pretreated catalyst was weighed into the reaction vessel and treated further in static H_2 for 1 h, followed by the addition of methanol as the reaction medium. Next, a known amount of freshly made CS_2 solution (8×10^{-5} M in methanol) was injected into the suspension, and H_2 treatment was completed under stirring for 45 min. The total volume of the liquid phase was 1 ml in each case. The substrate was then introduced to give S:Pd = 200 (mol/mol), and the reaction was left to proceed under vigorous stirring (1400 rpm) at 298 K at a constant pressure of 105 kPa. The H_2 consumption was monitored continuously during the reaction. The above procedure was repeated with increasing amounts of CS_2 until hydrogenation ceased. Fresh catalyst samples were used in each run. Blank experiments indicated that the extent of adsorption of CS_2 on the support material was negligible; the rate did not change when additional Al_2O_3, free of Pd, was present in the reaction system.

2.2.6. *Transmission electron microscopy*

Particle size analysis was performed with a Philips CM-10 transmission electron microscope operated at 100 kV and equipped with a Megaview II digital camera. TEM images were recorded for both H_2-treated (423 K for 4 h) and methanol-treated catalysts. Samples were prepared by placing a drop of a suspension of Pd/γ-Al_2O_3 in *n*-hexane or methanol onto a standard Cu grid covered by a thin Formvar layer, then evaporating off the solvent in air at room temperature. The size distribution of the Pd particles was determined using Analysis 3.1 software.

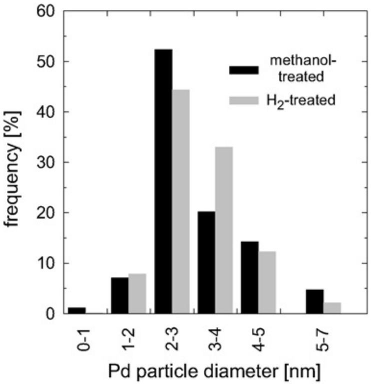

Fig. 3. Particle size distribution of Pd/γ-Al_2O_3 for samples pretreated in a H_2 flow and in methanol.

3. Results and discussion

The size distributions of the Pd particles before and after methanol treatment are displayed in Fig. 3. The two histograms relate to the catalyst samples used in the gas-phase and solution-phase experiments, respectively. No significant restructuring of the native particles was observed on exposure to methanol. By counting ca. 400 particles, the number-length mean diameters were determined to be 3.1 ± 0.8 nm for the H_2-treated samples and 2.9 ± 0.8 nm for the methanol-treated samples. Based on these observations, the apparent dispersion of the catalyst can be estimated as $D_{\mathrm{TEM}} = 100/d\ (\mathrm{nm}) = 33\%$ [21].

Recently, the applicability of LC in the proposed arrangement (Fig. 1) was demonstrated in pulsed-flow microcalorimetric studies on the nonreversible adsorption of various surfactants at the graphite–water interface [17,18]. Fig. 4 plots the cumulative CS_2 uptake by the catalyst plotted against the number of CS_2 pulses. The chemisorption capacity is reached at a saturation value of 5.2 mol of CS_2 per 100 mol of total Pd. This value can be transformed to a liquid-phase dispersion as $D_{\mathrm{L}}\ (\%) = 5.2 \times f$, where f is the Pd/CS_2 adsorption stoichiometry molecular ratio. In a recent review of CS_2 catalyst poisoning, including an analysis of the literature relating to the metal to CS_2 stoichiometry issue, the metal/CS_2 ratios were found to fall in two major groups, 2 or 4–6 [4]. Furthermore, most of the available structures of small-molecule organometallic complexes containing CS_2 have a ratio of $f = 2$ [4]. These observations suggest that a choice of $f = 2$ for the adsorption of CS_2 on Pd/γ-Al_2O_3 is adequate, which results in $D_{\mathrm{L}} = 10.4\%$.

Calorimetric studies on the adsorption of CO and H_2 on Pd/γ-Al_2O_3 offer further alternatives for the determination of D or, more specifically, D_{G}. Fig. 5 displays the results of gas-phase adsorption microcalorimetry. The initial differential

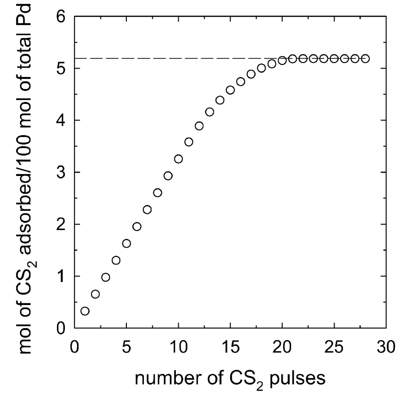

Fig. 4. Determination of the CS_2 uptake of 5 wt% Pd/γ-Al_2O_3 catalyst by liquid chromatography. The experimental response curve is given in Fig. 2.

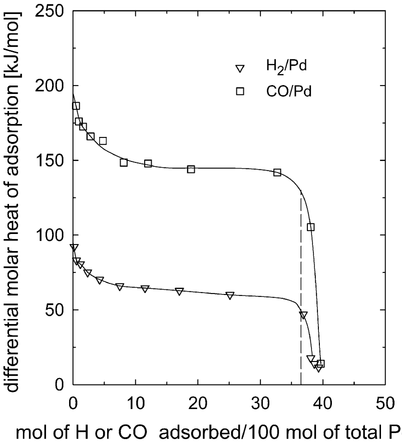

Fig. 5. Differential heats of chemisorption of H_2 and CO on 5 wt% Pd/γ-Al_2O_3 catalyst at 328.15 K. Chemisorption appears to be complete at the dashed line, after which weakly-bound surface species are formed.

heats of adsorption are $q_{\mathrm{ads}} = 195$ kJ/mol for CO and $q_{\mathrm{ads}} = 95$ kJ/mol H for the dissociative adsorption of H_2. These values are higher than the integral heats of adsorption of CO and H_2 reported in a review of numerous supported Pd catalysts [22], including Pd/γ-Al_2O_3. However, integral heats are average values for a large extent of surface coverage and do not furnish information about surface heterogeneity. Differential heats, in turn, reflect the site strength distribution of the catalyst. As adsorption proceeds, surface sites are occupied sequentially, depending on the magnitude of q_{ads}, with a declining slope until a pseudoplateau is reached at 145 kJ/mol for CO and 60 kJ/mol for H. As shown in Fig. 5, chemisorption appears to be complete at the knee positioned at 36 for both CO and H (mol/100 mol of total Pd), after which weakly bound surface species are formed, and q_{ads} drops sharply. For H_2 adsorption, the pronounced decrease in q_{ads} is associated with the formation of subsurface hydrogen, followed by the absorption of H_2 to produce an interstitial solid solution [23]. However, H_2 sorption in the pressure range of Pd-hydride formation was not of interest in the present study. Applying the adsorption stoichiometries of Pd/CO = 1 and Pd/H = 1 proposed for Al_2O_3-supported Pd nanoparticles [24,25], the gas-phase dispersion of the catalyst may be given as $D_{\mathrm{G}} = 36\%$.

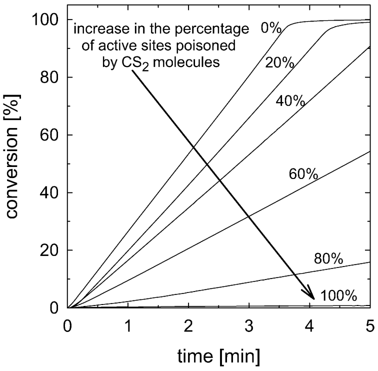

Fig. 6. A series of kinetic curves for the conversion of styrene to ethylbenzene on 5 wt% Pd/γ-Al_2O_3 catalyst (solvent, methanol; temperature, 298 K; pressure, 105 kPa H_2; styrene:Pd = 200 mol/mol).

It is difficult to decide which of the different experimental protocols can provide the number of surface sites that are actually active during reaction. The percentage of exposed metal atoms determined at the solid–gas interface in traditional chemisorption experiments or at the solid–solution interface by the present LC method may differ from the percentage of catalytically active surface sites at the solid–solution interface under given reaction conditions. The diversity of the experimental methods available and the different results obtained encouraged us to cross-check D in a test reaction in which the active sites of the catalyst were progressively blocked by CS_2 molecules and the number of these molecules was counted until the reaction ceased. The hydrogenation of styrene to ethylbenzene in methanol solution was selected for this catalytic probe. This reaction follows zero-order kinetics with respect to styrene throughout the entire range of conversion [12,14,26]. Experimentally, this kind of kinetic behavior implies a linear curve (conversion vs time), which rules out the possibility of gradual activation or deactivation of the catalyst due to the rearrangement of surface metal atoms or the formation of carbonaceous residues. Furthermore, the reaction conditions chosen for the catalytic probe closely mimic the conditions used in the LC experiment. Fig. 6 shows a series of the results of the kinetic experiments. The kinetic curves are linear over a large range of conversion, in accordance with zero-order kinetics [12,14,26]. The slopes of the curves decrease with increasing poisoning. The reaction rates calculated from the slopes of the straight lines were normalized with respect to the rate measured on the nonpoisoned catalyst. The relative rate of reaction defined in this way decreased from 1 to 0 as the fraction of the poisoned active sites increased from 0 to 1. The straight line in Fig. 7 denotes the relative rates of reaction at different levels of poisoning. The reaction rate becomes zero at the intercept of the line with the X axis; the active Pd sites are fully blocked at 5.8 mol of CS_2 per 100 mol of total Pd to give $D_{\mathrm{L}} = 11.6\%$ provided that two active sites are deactivated by one CS_2 molecule ($f = 2$).

The result of the catalytic probe is intrinsically consistent with the results of the LC study. The average value of the two liquid-phase dispersion data is $D_{\mathrm{L}} = 11.0 \pm 0.6\%$, which is far lower than the $D_{\mathrm{G}} = 36\%$ and $D_{\mathrm{TEM}} = 33\%$ determined by

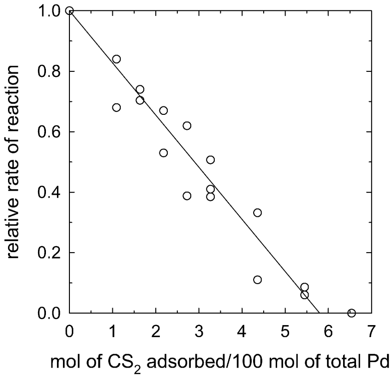

Fig. 7. Rates of hydrogenation of styrene to ethylbenzene on 5 wt% Pd/γ-Al_2O_3, relative to the rate on the nonpoisoned catalyst, at various fractions of active sites poisoned.

traditional methods under nonwet conditions. We offer two alternative explanations for the anomaly relating to the marked difference between the values of D_L and D_G. First, it can be argued that the selected stoichiometry of $f = 2$ is not correct even if a clear majority of previous studies are in favor of this choice. In fact, the main conflict can be readily resolved if it is assumed that 1 CS_2 molecule inactivates 6 Pd atoms on the surface ($f = 6$). With this assumption, the percentage of active sites determined in the liquid phase can be converted to $D_L = 6 \times 5.5 = 33\%$, which is in good agreement with D_G and D_{TEM}.

With the acceptance of $f = 2$, however, the maximum amount of CS_2 adsorbed from methanol solution results in a surface coverage far less than a monolayer, in a further contrast with the gas-phase adsorption of CS_2 on Pd films, which produced a surface coverage close to a monolayer [27]. Thus, the difference between D_G and D_L may be considered an indication that the number of exposed metal atoms at the solid–gas interface determined in chemisorption experiments is less than the number of active surface sites at the solid–solution interface. This statement is supported by the results of a recent study on a 5 wt% Rh/Al_2O_3 catalyst, in which the chemisorption capacities were found to be 3.5 mol for CS_2 and 33 mol for both CO and H per 100 mol of total Rh for adsorption at the solid–solution and solid–gas interfaces, respectively [4]. The relation $D_L < D_G$ can be explained by taking into consideration that although single-component gas adsorption is not competitive, adsorption from solution is a displacement process in which the solute and the solvent molecules compete for the surface sites. Thus, it may well occur that only a fraction of the surface sites are accessible for the reactant molecules. The remainder of the Pd surface atoms remains covered by solvent molecules, and hence these sites are not involved in the catalytic reaction.

4. Conclusions

We have described a CS_2-pulse LC method and applied it to measure the fraction of active sites of supported Pd nanoparticles (5 wt% Pd on γ-Al_2O_3) in methanol solution. The agreement between the results of CS_2 catalyst poisoning and the proposed LC method (5.2 and 5.8 mol of CS_2 per 100 mol of total Pd, respectively) is noteworthy. These independent experimental results are free of assumptions; however, the conversion of the results to D_L, the liquid-phase dispersion of the metal, is critically dependent on the value of f, the metal/CS_2 stoichiometry ratio. Two plausible values taken from the literature were considered: (i) for $f = 6$, $D_L = 33\%$, in good agreement with the $D_G = 36\%$ obtained from gas-phase calorimetry measurements (adsorption of CO and H_2) and and $D_{TEM} = 33\%$ obtained from TEM; and (ii) for $f = 2$, $D_L = 11\%$, indicating that gas-phase dispersion measurements appreciably overestimate the number of surface sites actually active in the liquid phase. This overestimation implies that the number of exposed metal atoms at the solid–gas interface is not equal to the number of active surface sites at the solid–solution interface. An important goal for future research will be to develop methods to measure the true metal/CS_2 stoichiometry ratios in solution.

Acknowledgments

This work was supported by the Bolyai János Foundation, Hungary; the Hungarian Scientific Research Fund (OTKA T042521 and T047390); the Turkish Scientific and Technical Research Council (TUBITAK MISAG 188); and the Alexander von Humboldt Foundation, Germany.

References

[1] P.N. Rylander, Hydrogenation Methods, Academic Press, New York, 1985.
[2] J.E. Benson, H.S. Hwang, M. Boudart, J. Catal. 30 (1973) 146.
[3] M. Boudart, Chem. Rev. 95 (1995) 661.
[4] B.J. Hornstein, J.D. Aiken III, R.G. Finke, Inorg. Chem. 41 (2002) 1625.
[5] C.A. Leon y Leon, M.A. Vannice, Appl. Catal. 69 (1991) 269.
[6] E. Díaz, S. Ordóñez, A. Vega, J. Coca, Chromatographia 61 (2005) 285.
[7] P. Canton, G. Fagherazzi, M. Battagliarin, F. Menegazzo, F. Pinna, N. Pernicone, Langmuir 18 (2002) 6530.
[8] L. Gonzalez-Tejuca, K. Aika, S. Namba, J. Turkevich, J. Phys. Chem. 81 (1977) 1399.
[9] S.-Y. Chen, B.J. McCoy, J.M. Smith, AIChE J. 32 (1986) 2056.
[10] I. Pálinkó, Stud. Surf. Sci. Catal. 88 (1994) 603.
[11] F. Notheisz, Á. Zsigmond, M. Bartók, Zs. Szegletes, G.V. Smith, Appl. Catal. A 120 (1994) 105.
[12] Z. Király, B. Veisz, Á. Mastalir, Catal. Lett. 95 (2004) 57.
[13] J.S. Bradley, W. Busser, Catal. Lett. 63 (1999) 127.
[14] B. Veisz, Z. Király, L. Tóth, B. Pécz, Chem. Mater. 14 (2002) 2882.
[15] D. Uner, N.A. Tapan, I. Özen, M. Uner, Appl. Catal. A 251 (2003) 225.
[16] D. Uner, M. Uner, Thermochim. Acta 434 (2005) 107.
[17] Z. Király, G.H. Findenegg, Á. Mastalir, J. Phys. Chem. B 107 (2003) 12,492.
[18] Z. Király, G.H. Findenegg, Langmuir 21 (2005) 5047.
[19] Z. Király, B. Veisz, Á. Mastalir, Gy. Kőfaragó, Langmuir 17 (2001) 5381.
[20] Á. Mastalir, Z. Király, J. Catal. 220 (2003) 372.
[21] W. Zou, R.D. Gonzalez, Catal. Lett. 12 (1992) 73.
[22] N. Cardona-Martinez, J.A. Dumesic, Adv. Catal. 38 (1992) 149.
[23] Z. Király, Á. Mastalir, F. Berger, I. Dékány, Langmuir 13 (1997) 465.
[24] R. Strobel, F. Krumeich, W.J. Stark, S.E. Pratsinis, A. Baiker, J. Catal. 222 (2004) 307.
[25] P. Chou, M.A. Vannice, J. Catal. 104 (1987) 1.
[26] G. Carturan, G. Facchin, G. Cocco, S. Enzo, G. Navazio, J. Catal. 76 (1982) 405.
[27] J.M. Saleh, Trans. Faraday Soc. 66 (1970) 242.