

Applications of adsorption microcalorimetry for the characterization of metal-based catalysts

Brian E. Spiewak, James A. Dumesic*

Department of Chemical Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

Abstract

Microcalorimetry is a useful tool for studies of heterogeneous catalysts, because it provides a direct measurement of the strength with which molecules interact with solid surfaces. The following communication reviews adsorption microcalorimetric studies of unsupported metals and metal-based catalysts performed over the last 20 years, and then presents three advanced microcalorimetric techniques and their applications to the study of low surface-area-metal single crystals, films and powders, and metal surfaces/catalysts that are highly reactive toward oxygenates. © 1998 Elsevier Science B.V.

Keywords: Adsorption; Catalysts; Microcalorimetry; Powders; Single crystals; Thin films; Transition metals

1. Introduction

Adsorption microcalorimetry has been widely used to measure the strength with which probe molecules adsorb on solid catalyst surface [1]. For example, many microcalorimetric studies have dealt with the adsorption of basic molecules (e.g. NH_3) on zeolites and metal oxide catalysts, to probe the strength of acid sites (see Ref. [1] and reference therein). In contrast, microcalorimetry has been used, to a lesser extent, for probing sites on metal-based catalysts, since reduced metal surfaces may be more susceptible to poisoning by trace oxygenates (e.g. O_2 , H_2O , CO and CO_2) present in high-vacuum systems. Thus, it is often difficult to prepare clean metal surfaces and maintain them in the zero-valence state for microcalorimetry.

New advances in adsorption microcalorimetry have made it possible to measure differential heats of adsorption on metal single crystals [2,3], polycrystalline metal films [4,5], and metal powders and metal-

based catalysts which are reactive toward oxygenates [6]. In this paper, we review selected microcalorimetric studies performed on supported and unsupported metals and, thereafter, present three advanced microcalorimetry techniques and their applications for the study of low surface area metals and metal-based catalysts.

2. Microcalorimetric studies of metal surfaces

Microcalorimetry has been used effectively to probe sites on supported-metal catalysts (e.g. Pt/ SiO_2) that are not overly sensitive to poisoning by oxygenates. The following is a brief summary of microcalorimetric studies performed on metal surfaces over the last 20 years.

Gravelle et al. were some of the first investigators to employ heat-flux or Tian–Calvet type calorimeters to measure heats of adsorption on supported metal catalysts [7–9]. Initial heats of 110 and 130 kJ/mol were reported for H_2 and CO adsorption, respectively, on

*Corresponding author.

silica-supported Ni catalysts at 296 K. Alloying Cu with Ni, however, decreased the initial heats and the saturation coverages for both CO and H₂ adsorption, suggesting that the presence of Cu weakens the interaction of these molecules with Ni.

Similar heat-flux microcalorimetric measurements were used to study strong metal–support interactions (SMSI) in Pt/TiO₂ catalysts [10], and to probe sites on supported Ir catalysts [11]. Initial heats of H₂ and CO adsorption at 296 K on Pt/TiO₂ were 93 and 130 kJ/mol, respectively. The initial heat of H₂ adsorption decreased to 80 kJ/mol, however, when strong metal–support interactions were present (i.e. after reducing the sample in H₂ at 773 K), suggesting that the reduced support modifies the chemical properties of Pt. Similarly, initial heats of CO adsorption at 296 K on silica- and Na–Y–zeolite-supported Ir catalysts were 148 and 120–140 kJ/mol, respectively, with higher heats of adsorption observed for Ir–Na–Y–zeolite resulting from higher sample reduction temperatures (e.g. 773 K).

Vannice et al. employed a modified differential scanning calorimeter (DSC) [12] to measure isothermal, integral heats of H₂, CO and O₂ adsorption on unsupported Pt powder (1600 nm) and on SiO₂-, SiO₂/Al₂O₃-, Al₂O₃-, and TiO₂-supported Pt catalysts, containing Pt crystallites ranging from 1–20 nm [13–18]. Adsorption of H₂ at 300 K yielded an average integral heat of 57 kJ/mol for all the catalysts studied, independent of the Pt crystallite size or the catalyst support. Adsorption of CO at 300 K yielded average integral heats in the 85–135 kJ/mol range, with poorly dispersed Pt/SiO₂ catalysts having the highest values and highly dispersed Pt/TiO₂ catalysts the lowest values. Average integral heats of O₂ adsorption at 300 K on Pt powder and well-dispersed Pt/SiO₂ were 220 and 285 kJ/mol, respectively, which suggests that the strength of the Pt–O interaction increases on small Pt crystallites.

A similar DSC study was performed on Pd powder (1000 nm) and SiO₂-, SiO₂/Al₂O₃-, Al₂O₃-, TiO₂-supported Pt catalysts, having Pd crystallites in the 1–12 nm range [19–23]. Average integral heats of H₂, CO and O₂ adsorption at 300 K were reported to vary in the 65–100, 90–145, and 210–335 kJ/mol ranges, respectively, independently of the catalyst support. The heats, however, increased significantly as the Pd crystallite size decreased below 3 nm for all the

catalysts studied, suggesting that small Pd crystallites strongly adsorb H₂, CO and O₂. Phillips et al. [24] have reported that the initial heats of H₂ adsorption at 300 K on similar Pd catalysts were 50–70 kJ/mol, depending on the support and the Pd particle size. Moreover, a recent DSC study of carbon-supported Pd [25] shows that the average integral heats for H₂, CO and O₂ adsorption in the 65–100, 70–90 and 190–230 kJ/mol ranges, respectively, which are lower (with the exception of H₂) than the corresponding values on oxide-supported Pd catalysts.

Differential scanning calorimetry was further used to measure heats of O₂, ethylene, and butadiene adsorption on Al₂O₃-supported Ag at 300 and 443 K [26]. Average integral heats of O₂ adsorption at 443 K are in the 140–210 kJ/mol range, with higher heats observed for smaller Ag crystallites. Heats of O₂ adsorption at 300 K were slightly lower, but exhibited the same dependence on crystallite size. Heats of ethylene and butadiene adsorption at 443 K were found to be 42 and 38 kJ/mol, respectively. At 300 K, the heats of ethylene and butadiene adsorption were indeterminate because of sizable heats (ca. 40–45 kJ/mol) contributed by adsorption of these molecules on the Al₂O₃ support.

Vannice et al. have also used a DSC to study carbon-supported Fe, Fe–Mn, Fe–K and K–Fe–Mn catalysts derived from stoichiometric mixed-metal carbonyl clusters [27,28]. Average integral heats of adsorption of CO at 300 K on Fe/C, Fe–Mn/C, Fe–K/C and K–Fe–Mn/C were 63, 72, 70 and 87 kJ/mol, respectively. These results showed that both Mn and K increase the heat of CO adsorption on Fe, and suggest that K and Mn are in contact with the Fe surface.

Recently, a DSC has been used to investigate Al₂O₃-supported Pt, Pt–Sn, and Pt–In catalysts [29,30]. Average integral heats of H₂ adsorption on Pt/Al₂O₃ at 300 K are in the 55–60 kJ/mol range, and decreased to 45–55 kJ/mol in the presence of Sn or In. Average integral heats of CO adsorption at 300 K were ca. 95 kJ/mol for all catalysts studied, independently of the presence of Sn and In. Average integral heats of ethylene adsorption at 300 K were ca. 90 kJ/mol on highly dispersed Pt catalysts having small Pt crystallites, and these heats were not altered by the presence of Sn or In. In contrast, heats of ca. 130 kJ/mol were measured on catalysts having larger Pt crystallites with no Sn or In. These results were interpreted by

noting that ethylene adsorbs dissociatively (i.e. as ethylidyne species) on large clusters of Pt atoms, and molecularly (i.e. as π - or di- σ -bonded ethylene) on smaller Pt clusters. In the absence of Pt, average integral heats of ethylene adsorption at 300 K were 21, 40 and 28 kJ/mol on Al_2O_3 , $\text{Sn}/\text{Al}_2\text{O}_3$ and $\text{In}/\text{Al}_2\text{O}_3$, respectively.

Phillips et al. have used heat-flux microcalorimetry to study high surface-area carbon [31–35]; graphite-supported Ir [36], Pd [24], Fe [37], Rh [38], Fe–Rh [39,40] and Fe–Pd [41,42] catalysts; and oxide-supported Fe, Fe–Rh [43] and Pd–Ag [44] catalysts. Initial heats of H_2 , CO and O_2 adsorption at 300 K on graphite-supported Ir particles were 70, 170 and 450 kJ/mol, respectively. Similar measurements of O_2 adsorption at 300 K on graphite-supported Fe, Rh, Fe–Rh and Fe–Pd catalysts yielded values of 600, 375, 540 and 520 kJ/mol, respectively. The Fe catalysts were reported to form bulk oxides, while O_2 chemisorption occurred on the Rh, Fe–Rh and Fe–Pd samples. The initial heats of O_2 adsorption were reduced significantly on silica-supported Fe, and silica- and alumina-supported Fe–Rh catalysts, to values of 420, 500 and 355 kJ/mol, respectively. Initial heats of 140–150 kJ/mol were reported for CO adsorption at 300 K on silica-supported Pd–Ag catalysts, due to change in catalyst morphology following different catalyst pre-treatments.

Dumesic et al. have used heat-flux microcalorimetry to study supported Pt [45–49], Pt–Sn [47–50], Pd [49], and Cu [51] catalysts, and unsupported Ni powder, Ni–B, and Ni–P [52] catalysts. Initial heats of 90 and 140 kJ/mol were reported for H_2 and CO adsorption at 403 K, respectively, for Pt supported on silica and non-acidic zeolites [45]. The initial heats were independent of Pt particle size for Pt loadings between 1 and 7 wt%, but were increased by ca. 20 kJ/mol when Pt was supported on basic materials such as K/SiO_2 , $\text{Mg}/\text{Al}_2\text{O}_3$, or zeolite containing basic cations (K^+ , Ba^{2+}). Exposure of the Pt/SiO_2 catalysts to reaction conditions for *n*-hexane aromatization (e.g. mixtures of *n*-hexane and H_2 at 700 K) resulted in a decrease in the total number of adsorption sites and a decrease in the number of sites that adsorb CO strongly [46]. In contrast, Pt supported in L-zeolite showed no change in the extent and heat of CO adsorption after exposure to reaction condition for *n*-hexane aromatization. The addition of Sn to Pt/SiO_2

catalysts decreased the number of sites that interact strongly with H_2 and CO [47]. Further addition of potassium to silica-supported Pt and Pt–Sn catalysts, increased the saturation extent of H_2 adsorption and decreased the saturation extent of CO adsorption, but did not affect the initial adsorption heats of these molecules [48]. The addition of Sn, and subsequent, addition of K to L-zeolite-supported Pt showed effects similar to those observed on silica-supported Pt [50].

Similar microcalorimetric measurements have been used to characterize the interaction of hydrocarbons with supported metal catalysts [47–49]. Initial heats of ethylene adsorption at 300 K on silica-supported, Pt, Pd and Pt–Sn catalysts were ca. 150, 170 and 120 kJ/mol, respectively. Initial heats of isobutylene adsorption at 300 K on these catalysts were ca. 160, 190 and 125 kJ/mol, respectively. The high values observed for silica-supported Pt and Pd were attributed to dissociative adsorption of ethylene and isobutane on these catalysts at 300 K to form alkylidyne species. In contrast, the lower heats observed on Pt–Sn/ SiO_2 , were attributed to the adsorption of π - or di- σ -bonded ethylene on Pt at 300 K. Accurate measurements of the heat of isobutane adsorption at 300 K on Pt and Pd/ SiO_2 were not possible due to extensive isobutane dehydrogenation. Initial heats, however, were in the 160–225 kJ/mol range, and were decreased in the presence of Sn.

Microcalorimetric measurements of CO, C_2H_4 , N_2O , O_2 adsorption at 313 K on Cu/SiO_2 and Cu–Y-zeolite have been used to probe the adsorption properties of metallic Cu and Cu^{1+} cations, respectively [51]. Initial heats of CO and C_2H_4 on Cu^{1+} cations (Cu–Y-zeolite) were 80 and 90 kJ/mol, respectively, while initial heats of CO and C_2H_4 on metallic Cu (Cu/SiO_2) were 64 and 60 kJ/mol, respectively. Oxygen, however, adsorbed more weakly with a strength of 95–170 kJ/mol on Cu^{1+} cations, as compared to the value of 400 kJ/mol for metallic Cu estimated from the heat of N_2O decomposition.

Heat-flux microcalorimetry was used to characterize unsupported Ni powder, and Ni–B and Ni–P alloy particles prepared by aqueous chemical reduction [52]. Initial heats of H_2 and CO adsorption on Ni at 303 K were 85 and 120 kJ/mol, respectively. The presence of B and P significantly increased the BET surface areas from the value of 1.7 m^2/g for Ni powder, to 8.4 and 19.7 m^2/g for Ni–B and Ni–P, respec-

tively. The presence of B and P, however, decreased the initial heats of H₂ and CO adsorption by 20–30 kJ/mol and, subsequently, reduced the saturation uptakes of these molecules per unit surface area. The decrease in the heats of H₂ and CO and adsorption were explained in terms of the electronegativity of the B and P metalloid elements.

King et al. have used heat-flux calorimetry to characterize the interaction of H₂ with silica-supported Ru, K–Ru and Ru–Ag catalysts [53,54]. Initial heats of H₂ adsorption at 403 K were ca. 90 kJ/mol for all Ru catalysts studied (including Ru black), independent of the K or Ag concentrations, suggesting that there is no electronic effect influencing H₂ chemisorption. The addition of K and Ag to Ru/SiO₂, however, significantly decreased the overall H₂ uptake, and the populations of intermediate (50 kJ/mol) and weakly (10 kJ/mol) bound hydrogen states observed at higher H₂ pressures.

Guil et al. have used microcalorimetry to investigate the adsorption of H₂ on SrTiO₂-supported Rh particles [55]. The Rh/SrTiO₂ system was used because H₂ adsorption was not appreciably affected by strong metal–support interactions (SMSI), and H₂ spillover onto the SrTiO₂ support is lower than for more reducible oxides (e.g. TiO₂). Initial heats of H₂ adsorption at 298 K on Rh/SrTiO₂ were ca. 40 kJ/mol, and decreased steadily until a constant value of 7 kJ/mol was reached, corresponding to the heat of H₂ adsorption on the SrTiO₂ support. The decrease in the strength of the H–Rh interaction with H₂ coverage was discussed on the basis of adsorption site heterogeneity and a modification of the electronic properties at the metal surface.

Stradella has investigated the interaction of several probe molecules with polycrystalline Ni powder using heat-flux microcalorimetry [56]. Initial heats of O₂, NH₃, N₂, N₂O, H₂, CO₂, C₃H₆, and CO adsorption at 305 K, were 75, 62, 55, 43, 40, 38, 14 and 10 kJ/mol, respectively, and remained constant at these values until the Ni surface became saturated. Oxygen, NH₃ and N₂ adsorption were the strongest and most irreversible, in contrast to C₃H₆ and CO adsorption which were weak and fully reversible. Thermokinetic calculations indicate that O₂, NH₃, N₂ and H₂ may undergo activated diffusion into bulk Ni.

In addition to microcalorimetric studies of metal-based catalysts, Cerny et al. have used a differential

isoperibolic (Beeck type) calorimeter [57] to measure differential heats of adsorption of H₂, CO, and several hydrocarbons at room temperature on evaporated metal films of Mo [57–60], Pt [58,61,62], Ce [63], Dy [63–65], Dy–Cu [65], Gd [66], Er [63], Lu [63], Tm [63] and Yb [63]. For example, initial heats of 90 and 40 kJ/mol were reported for H₂ adsorption on evaporated Pt and Mo films, respectively. Similarly, initial heats of 148 and 280 kJ/mol were reported for ethylene adsorption, and initial heats of 187 and 275 kJ/mol were reported for acetylene adsorption on these same films, respectively.

3. Advances in microcalorimetry for metals

The difficulty in maintaining clean metal surfaces complicates the use of microcalorimetric methods to study adsorption phenomena on metals. Recent advances in microcalorimetry, however, have provided a means to study low surface area metal single crystals and films, unsupported metal powders, and metal-based catalysts which may be contaminated by oxygenates. The following section presents three advance microcalorimetric techniques and their applications toward the study of low surface area metals and metal-based catalysts. For more detailed information regarding adsorption microcalorimetry in surface science studies, the reader is referred to a recent, comprehensive review by Cerny [67].

King et al. have developed an ultrahigh vacuum microcalorimeter, capable of measuring absolute heats of adsorption as a function of adsorbate coverage on low surface-area metal single-crystal surfaces [2,3,68]. The calorimeter consists of a pulsed supersonic molecular beam source, an ultrathin (ca. 2000 Å) metal single crystal, and remote infrared temperature sensing. In a typical experiment, a 2000 Å thick, 1-cm² metal single crystal is supported within an ultrahigh vacuum chamber and, subsequently, cleaned by Ar-ion sputtering. The adsorbate gas is dosed via pulsed molecular beam onto an unsupported circular section of the crystal (ca. 2 mm in diameter), such that heat losses are by radiation only. A broadband infrared photon detector, placed directly behind the crystal, records the infrared emission (heat) radiated from the back of the crystal face during each pulse, which is directly proportional

to the heat of adsorption. The adsorbate uptake is then determined for each pulse from the product of the number of molecules incident on the sample (related to the beam intensity) and the fraction that are adsorbed (the sticking probability, calculated using the method of King and Wells [69]). This calorimeter has a sensitivity to adsorption of 0.01 monolayers of adsorbate, and it has been used to measure heats of adsorption on various Ni [2,3,68,70–75] and Pt [68,76–81] crystal planes.

Heats of CO and O₂ adsorption at 300 K have been measured on the (100), (110) and (111) planes of clean and K-promoted Ni [70–73]. Initial heats of CO adsorption on Ni(100), Ni(110) and Ni(111) were 123, 133 and 130 kJ/mol, respectively, while initial heats of dissociative O₂ adsorption on the same crystal planes were 532, 498 and 470 kJ/mol, respectively. The addition of potassium to the Ni single crystals, however, significantly increased the heats of adsorption of these molecules. For example, addition of 0.08 monolayers of K to Ni(100) increased the initial heats of CO and O₂ adsorption to 170 and 620 kJ/mol, respectively, and the addition of 0.30 monolayers of K to Ni(100), increased the initial heats to 250 and 590 kJ/mol, respectively. These results indicate that the presence of K on Ni(100) increases the strengths of the Ni–CO and Ni–O bonds, which have been explained in terms of increased electron density at the Ni surface. Similarly, an initial heat of 426 kJ/mol has been measured for dissociative NO adsorption on Ni(100) at 300 K [75], and this value, along with the corresponding value for dissociative O₂ adsorption, has been used to estimate a heat of 136 kJ/mol for dissociative N₂ adsorption on Ni(100).

The ultrahigh vacuum single-crystal adsorption calorimeter has also been used to measure heats of CO, O₂, NO and C₂H₄ adsorption on Pt single crystals [76–79,81], and to measure the heat of the reaction for CO oxidation on Pt [80]. The adsorption of C₂H₄ on Pt(110)-(2×1) at 300 K yielded four distinct regions of differential heat vs. coverage, having values of 205, 170, 136 and 120 kJ/mol, which were assigned to ethylidyne (≡CCH₂-), ethylidyne (≡CCH₃), di-σ-bonded ethylene (-H₂CCH₂-), and π-bonded ethylene species, respectively [76]. Initial heats of C₂H₄ adsorption at 300 K on Pt(111) [78] and the hexagonal and (1×1) phases of Pt(100) [77] were 174, 200 and 250 kJ/mol, respectively, indicating that different

crystal planes and different surface phases affect the interaction of C₂H₄ with Pt. Similarly, the initial heats of CO adsorption at 300 K on Pt(110) [81] and the hexagonal and (1×1) phases of Pt(100) [77,79] were 183, 180 and 225 kJ/mol, respectively, and the initial heats of NO adsorption at 300 K were 160, 180 and 200 kJ/mol, respectively, suggesting that different crystal planes and different surface phases also affect the interaction of CO and NO with Pt. Comparison of the heats of C₂H₄, CO, and NO adsorption on Pt(100), shows that the energy difference between the hexagonal and (1×1) phases is ca. 20 kJ/mol [77]. The adsorption of O₂ at 300 K on Pt(100) [81] gave an initial heat of 335 kJ/mol.

King et al. [74] have expanded the applicability of the single-crystal adsorption calorimeter by developing a pyroelectric temperature sensor for measuring absolute heats of adsorption at low temperatures. The sensor consists of a pyroelectric LiTaO₃ wafer connected by electrodes to a high-impedance amplifier, forming a parallel plate capacitor. A metal single crystal is cold welded to the surface of the LiTaO₃ wafer to provide good heat transfer. Since pyroelectric materials have a permanent, temperature-dependent electric polarization along a particular crystalline axis, these materials exhibit a change in polarization with temperature, which can be correlated to measurable voltage changes. Thus, a temperature change induced by the adsorption of a probe molecule on a single-crystal surface, results in voltage change across the capacitor, which is proportional to the heat of adsorption. This pyroelectric detection scheme has been used successfully with the single-crystal adsorption calorimeter to measure heats of O₂ adsorption on Ni(100) at 300 K (ca. 530 kJ/mol) and 110 K (ca. 480 kJ/mol). The lower heat of adsorption measured at 100 K has been attributed to reduced mobility of adsorbed oxygen at this temperature.

A similar calorimeter, employing a pulsed molecular-beam source and a pyroelectric LiTaO₃ single crystal as a temperature sensor, has been developed independently by Cerny et al. [4,5], for measuring heats of adsorption on thin metal films. In their apparatus, a thin metal film is evaporated onto the surface of a LiTaO₃ single crystal, and then pulsed with adsorbate via the molecular beam. Absolute heats of adsorption are then determined through voltage changes in the LiTaO₃ single crystal, and the adsorbate

coverages are calculated from the product of the sticking coefficient and the number of molecules incident on the sample, as in the method of King et al. [74]. The present calorimeter has been used to measure initial heats of 265 and 670 kJ/mol for CO and O₂ adsorption, respectively, on an evaporated Dy film at room temperature.

We have developed a technique for using conventional heat-flux microcalorimeters to measure differential heats of adsorption of probe molecules on unsupported metal powders and metal-based catalysts which are reactive toward oxygenates [6]. Clean, reduced metal samples are prepared *ex situ*, in a down-flow glass treatment cell, using ultrapure flowing gases. The reduced metal sample is then sealed in pure helium within a Pyrex NMR tube attached to the side of the glass treatment cell. The sample capsule formed in this manner, is broken in a special set of microcalorimetric cells, shown schematically in Fig. 1. The cells, equipped with Cajon VCR high-vacuum fittings, employ a bellows-sealed linear motion feed-through to drive a rod into the sample receptacle to break the sealed Pyrex sample capsule. In this manner, the clean sample can be exposed rapidly to the adsorbate gases under study, without excessive surface contamination that can accumulate during the long periods (ca. 5–6 h) required for thermal equilibration of the sample in the calorimeter.

The present microcalorimetric technique has been used to probe the interaction of H₂ and CO with Ni powders containing submonolayer amounts of metallic K and Cs [82]. Fig. 2 shows results for CO adsorption at 308 K on clean Ni powder and Ni powders containing both, metallic and oxidized K and Cs adatoms. The adsorption of H₂ and CO on reduced Ni powder at 308 K, gave initial heats of 90 and 120 kJ/mol, respectively. The addition of metallic K (0.1–0.2 monolayers) and Cs (0.3–0.6 monolayers) to Ni powder, significantly increased the initial heats of CO adsorption to ca. 200 kJ/mol. Exposure of these samples to air, and subsequent reduction in H₂ at 673 K, however, reduced the initial heats of CO adsorption to ca. 160 kJ/mol. In contrast, the addition of K had weaker promotional effects on the adsorption of H₂. Initial heats of 110 and 100 kJ/mol were measured for H₂ adsorption at 308 K on Ni powder containing metallic and oxidized K atoms, respectively. These results show that the presence of metallic

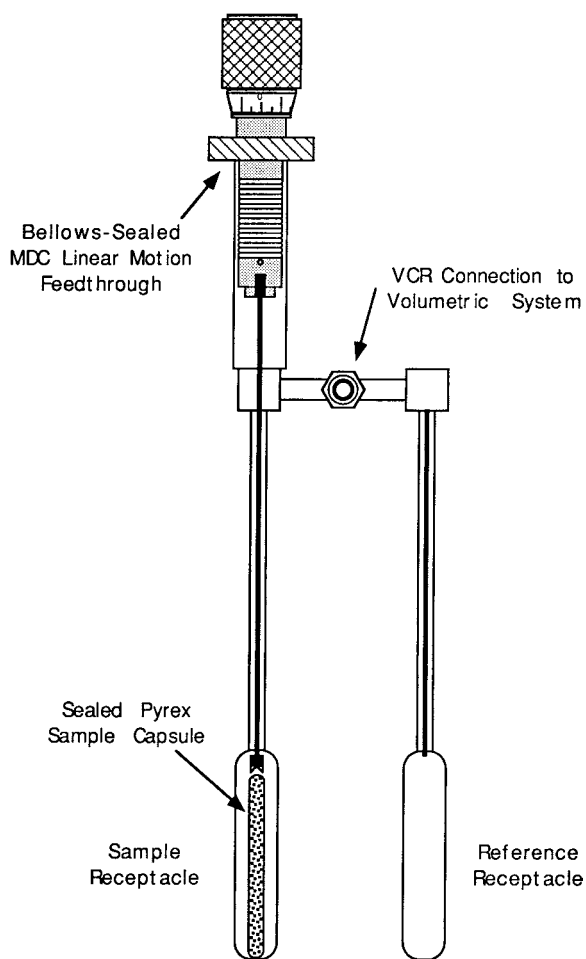


Fig. 1. Schematic diagram of the microcalorimetric cell.

alkali promotes the adsorption of CO, and to a lesser extent, H₂ on Ni, by increasing the strengths of the Ni–CO and the Ni–H bonds. Oxidation of the alkali species, however, moderates these promotional effects. Importantly, the results for CO adsorption on both clean and metallic K-promoted Ni powders are in excellent agreement with similar measurements performed by King et al. [70] on clean and K-promoted Ni(100), and indicate that the present methods are effective for preparing clean, reduced Ni surfaces containing alkali metals, and maintaining these surfaces in the zero-valence state for microcalorimetry.

A similar microcalorimetric study was conducted on Pt powders and silica-supported Pt and Pt–Sn catalysts containing alkali metals, to address the che-

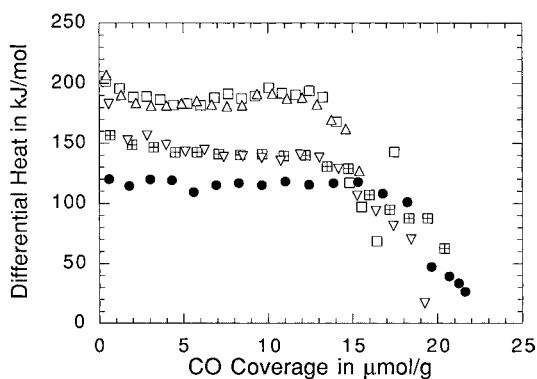


Fig. 2. Microcalorimetric results of CO adsorption at 308 K on Ni powder (●), K-promoted Ni (□), Cs-promoted Ni (△), and the K-promoted (⊗) and Cs-promoted (▽) Ni samples after exposure to air, and subsequent reduction in H₂ at 673 K

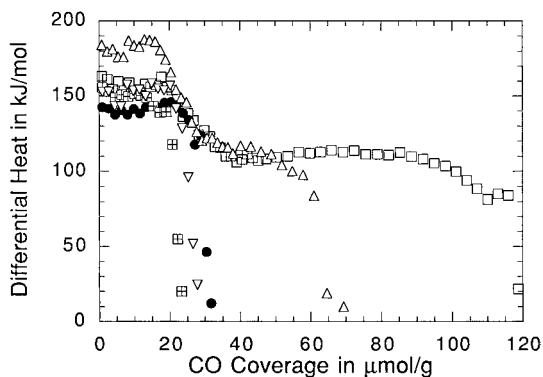


Fig. 3. Microcalorimetric results of CO adsorption at 403 K on Pt powder (●), Rb-promoted Pt (□), Cs-promoted Pt (△), and the Rb-promoted (⊗) and Cs-promoted (▽) Pt samples after exposure to air, calcination in O₂ at 473 K, and subsequent reduction in H₂ at 373 K.

mical state and role the alkali metals as catalytic promoters for the dehydrogenation of isobutane [83]. Fig. 3 shows results for CO adsorption at 403 K on clean Pt powder and Pt powders containing both, metallic and oxidized Rb and Cs adatoms. Microcalorimetric measurements of CO adsorption at 403 K yielded an initial heat of 140 kJ/mol and a CO saturation coverage of 30 μmol/g. The addition of metallic Rb (0.1–0.4 monolayers) and Cs (0.6–0.8 monolayers) to Pt, increased the initial heats of CO adsorption to 160 and 180 kJ/mol, respectively, and extended the CO adsorption capacity to 110 and 60 μmol/g, respectively. Exposure of these samples

to air, followed by calcination in O₂ at 473 K and, subsequent, reduction in H₂ at 373 K, however, eliminated the promotional effects, resulting in initial heats and saturation CO coverages similar to those obtained on clean Pt. These results show the presence of metallic Rb and Cs on Pt promotes the adsorption of CO, by strengthening the Pt–CO bonds and extending the CO adsorption capacity, while oxidized alkali species have little effect on CO adsorption. The increase in the CO adsorption capacity observed for Pt powders containing metallic Rb and Cs, resulted from formation of an alkali–CO complex on Pt at 403 K.

Microcalorimetric measurements of CO adsorption on silica-supported Pt (0.85 wt% Pt) and Pt–Sn (2.61 wt% Pt) catalysts at 403 K, gave initial heats of 140 and 120 kJ/mol and CO saturation coverages of 25 and 65 μmol/g, respectively. The addition of K, Rb and Cs salts (1 : 5 atomic Pt : alkali) to Pt/SiO₂ followed by treatment in H₂ at 773 K, did not affect the adsorption of CO at 403 K. In contrast, the addition of Na and Cs salts (1 : 3 atomic Pt : alkali) to Pt–Sn/SiO₂ followed by treatment in H₂ at 773 K, resulted in a significant decreases in the CO saturation coverage. Comparison of the results for supported and unsupported Pt, suggests that the alkali are not in the metallic state on working silica-supported Pt and Pt–Sn isobutane dehydrogenation catalysts, and that the promotional effects observed for alkali-promoted Pt–Sn/SiO₂ are the result of alkali species decreasing the ensemble size of surface Pt sites.

The present microcalorimetric technique has also been used to investigate the interaction of N₂ with Fe–ammonia synthesis catalysts [6,84]. Initial heats of ca. 200 kJ/mol have been measured for dissociative N₂ adsorption at 453 and 673 K on various iron-based catalysts. Importantly, these heats are in excellent agreement with heats of 200–230 kJ/mol estimated from ultrahigh vacuum measurements of N₂ desorption from Fe single crystals [85–87].

In a recent work, the present microcalorimetric technique has been employed to investigate the interaction of C₂H₄ and H₂ at 173 K on clean Pt surfaces, and on Pt surfaces that have undergone C₂H₄ hydrogenation at 330 K [88]. Fig. 4 shows the results for C₂H₄ adsorption at 303 and 173 K on clean Pt powder, and at 173 K on Pt powder that has undergone ethylene hydrogenation at 300 K under conditions, where

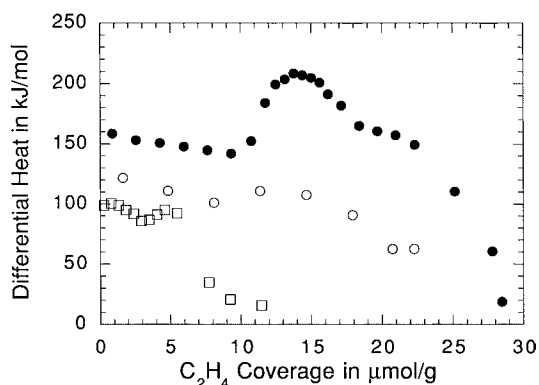


Fig. 4. Microcalorimetric results of C_2H_4 adsorption at 303 (●) and 173 K (○) on Pt powder, and at 173 K (□) on Pt powder that has undergone ethylene hydrogenation at 300 K under conditions, where ethylidyne species form.

ethylidyne species are present. Microcalorimetric measurements of C_2H_4 adsorption on reduced Pt powder at 303 and 173 K gave initial heats of 160 and 120 kJ/

mol, respectively, in excellent agreement with values obtained by King et al. [76,78] for C_2H_4 adsorption on Pt single crystals. These strengths of adsorption correspond to ethylidyne species and to di- σ -bonded ethylene, respectively. The increase in differential heat with coverage observed for C_2H_4 adsorption at 300 K (Fig. 4), was a result of C_2H_6 formation. Initial heats measured for H_2 adsorption on reduced Pt powder at 403 and 173 K were ca. 90 kJ/mol. Exposure of the Pt samples to C_2H_4 hydrogenation at 300 K, under conditions at which ethylidyne species form, results in a significant decrease in the strengths (20–30 kJ/mol) as well as the saturation coverages of C_2H_4 and H_2 adsorption at 173 K. Exposure of Pt to C_2H_4 hydrogenation at conditions for which ethylidyne species do not form results in a similar decrease in the adsorption strength and the saturation uptake of H_2 at 173 K. However, these surfaces contain significant amounts of reactive hydrogen, since they show formation of C_2H_6 upon C_2H_4 adsorption at 173 K. In short, these

Table 1
Calorimetric heats of H_2 , CO, O_2 and C_2H_4 adsorption on Ni and Pt

Metal	H_2 / kJ/mol	CO/ kJ/mol	O_2 / kJ/mol	C_2H_4 / kJ/mol	Temperature/ K	Calorimetry type	References
Ni(100)		123	532		300	SCAC ^a	[70–73]
			480		100	SCAC ^a	[74]
Ni(110)		133	498		300	SCAC ^a	[70–73]
Ni(111)		130	470		300	SCAC ^a	[70–73]
Ni powder	85	120			303	HFC ^b	[52]
	40	10	75		305	HFC ^b	[56]
	90	120			303	RMHFC ^c	[82]
				130	173	RMHFC ^c	[89]
Ni/SiO ₂	110	130			296	HFC ^b	[7–9]
Pt(100)-hex		180		200	300	SCAC ^a	[77,79]
Pt(100)-1×1		225		250	300	SCAC ^a	[77,79]
Pt(100)-2×1		183	335	205	300	SCAC ^a	[76,81]
Pt(111)				174	300	SCAC ^a	[78]
Pt film	90			148	295	TFC ^d	[58,61–72]
Pt powder	57	113	220		300	DSC ^e	[16–18]
	90	140			403	RMHFC ^c	[83,88]
				160	303	RMHFC ^c	[88]
				120	173	RMHFC ^c	[88]
Pt/SiO ₂	57	123	285		300	DSC ^e	[16–18]
	90	140			403	HFC ^b	[45,57]
				150	300	HFC ^b	[47–49]
		140			403	RMHFC ^c	[83]

^a Single-crystal adsorption calorimetry.

^b Heat-flux calorimetry.

^c Reactive metal heat-flux.

^d Thin-film calorimetry (isoperibolic calorimeter).

^e Differential scanning calorimetry.

experiments provide thermodynamic and kinetic information about reactive surface intermediates on both clean and working Pt surfaces.

In related work, the present microcalorimetric technique has been used to probe the interaction of C₂H₄ and C₂H₂ with Ni, Pt, and Pd powders [89]. Initial heats of 130 and 250 kJ/mol have been measured for C₂H₄ and C₂H₂ adsorption, respectively, on reduced Ni powder at 173 K. Initial heats of 225 and 200 kJ/mol have been measured for C₂H₂ adsorption on reduced Pt powder at 303 and 173 K, respectively. Similarly, initial heats of 180 and 140 kJ/mol have been measured for C₂H₄ adsorption on reduced Pd powder at 303 and 173 K, respectively, which correspond to ethylidyne species and to di- σ -bonded ethylene, respectively. In addition, an initial heat of 145 kJ/mol has been measured for CO adsorption on Pd powder at 403 K [89].

Of the numerous calorimetric studies reviewed in the present paper, the majority of these studies have focused on the adsorption of simple probe molecules on Ni and Pt surfaces. For the purpose of comparison, the heats of H₂, CO, O₂ and C₂H₄ adsorption obtained on various Ni and Pt surfaces with different microcalorimetric methods, have been summarized in Table 1. A more complete table of differential heats of adsorption of various probe molecules on metal single crystals, and polycrystalline metal wires, ribbons, and films can be found in Ref. [67].

4. Conclusions

Microcalorimetry is a powerful technique for measuring the strength with which adsorbates interact with solid catalyst surfaces. Moreover, recent developments in microcalorimetry have provided means to extend these measurements to metal single crystals, metal films, metal powders, and metal-based catalysts which are reactive toward oxygenates. These microcalorimetric methods have provided new insight into the interaction of adsorbates with metal surfaces and will advance the study of metal-based catalyst systems.

Acknowledgements

Funding for this work has been provided by the National Science Foundation and Haldor Topsøe A/S.

Special thanks are extended to Randy Cortright, Jianyi Shen, Per Levin, Manuel Natal-Santiago, Josie Hill, and Erik Haralson, for help with the experiments performed in these studies.

References

- [1] B.E. Spiewak, R.D. Cortright, J.A. Dumesic, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis*, vol. A, in press, 1997.
- [2] C.E. Borroni-Bird, D.A. King, *Rev. Sci. Instrum.* 62 (1991) 2177.
- [3] C.E. Borroni-Bird, N. Al-Sarraf, S. Andersson, D.A. King, *Chem. Phys. Lett.* 183 (1991) 516.
- [4] M. Kovár, L. Dvorák, S. Cerny, *Appl. Surf. Sci.* 74 (1994) 51.
- [5] L. Dvorák, M. Kovár, S. Cerny, *Thermochim. Acta* 245 (1994) 163.
- [6] B.E. Spiewak, J.A. Dumesic, *Thermochim. Acta* 290 (1997) 43.
- [7] J.J. Prinsloo, P.C. Gravelle, *J.C.S. Faraday I* 76 (1980) 512.
- [8] J.J. Prinsloo, P.C. Gravelle, *J.C.S. Faraday I* 76 (1980) 2221.
- [9] J.J. Prinsloo, P.C. Gravelle, *J.C.S. Faraday I* 78 (1982) 273.
- [10] J.M. Herrmann, M. Gravelle-Rumeau-Maillot, P.C. Gravelle, *J. Catal.* 104 (1987) 136.
- [11] P. Gelin, A. Auroux, Y. Ben Taarit, P.C. Gravelle, *Appl. Catal.* 46 (1989) 227.
- [12] M.A. Vannice, B. Sen, P. Chou, *Rev. Sci. Instrum.* 58 (1987) 647.
- [13] M.A. Vannice, L.C. Hasselbring, B. Sen, *J. Catal.* 95 (1985) 57.
- [14] M.A. Vannice, L.C. Hasselbring, B. Sen, *J. Phys. Chem.* 89 (1985) 2972.
- [15] M.A. Vannice, L.C. Hasselbring, B. Sen, *J. Catal.* 97 (1986) 66.
- [16] B. Sen, P. Chou, M.A. Vannice, *J. Catal.* 101 (1986) 517.
- [17] B. Sen, M.A. Vannice, *J. Catal.* 130 (1991) 9.
- [18] B. Sen, M.A. Vannice, *J. Catal.* 129 (1991) 31.
- [19] A. Vannice, P. Chou, *J. Chem. Soc., Chem. Commun.* 23 (1984) 1590.
- [20] M.A. Vannice, P. Chou, *ACS Symp. Ser.* 298 (1986) 76.
- [21] P. Chou, M.A. Vannice, *J. Catal.* 104 (1987) 1.
- [22] P. Chou, M.A. Vannice, *J. Catal.* 104 (1987) 17.
- [23] P. Chou, M.A. Vannice, *J. Catal.* 105 (1987) 342.
- [24] R.W. Wunder, J.W. Cobes, J. Phillips, L.R. Radovic, A.J. Lopez-Peinado, F. Carrasco-Marin, *Langmuir* 9 (1993) 984.
- [25] N. Krishnankutty, M.A. Vannice, *J. Catal.* 155 (1995) 312.
- [26] K.L. Anderson, J.K. Plischke, M.A. Vannice, *J. Catal.* 128 (1991) 148.
- [27] J.J. Venter, A.A. Chen, J. Phillips, M.A. Vannice, *J. Catal.* 119 (1989) 451.
- [28] J.J. Venter, M.A. Vannice, *Catal. Lett.* 7 (1990) 219.
- [29] F.B. Passos, M. Schmal, M.A. Vannice, *J. Catal.* 160 (1996) 106.
- [30] F.B. Passos, M. Schmal, M.A. Vannice, *J. Catal.* 160 (1996) 118.

- [31] M. O'Neil, R. Lovrien, J. Phillips, *Rev. Sci. Instrum.* 56 (1985) 2312.
- [32] M. O'Neil, J. Phillips, *J. Phys. Chem.* 91 (1987) 2867.
- [33] A.S. Gow III, J. Phillips, *Energy Fuels* 6 (1992) 526.
- [34] A.S. Gow, J. Phillips, *Energy Fuels* 6 (1993) 184.
- [35] A.S. Gow, J. Phillips, *Energy Fuels* 7 (1993) 674.
- [36] J. Cobes, J. Phillips, *J. Phys. Chem.* 95 (1991) 8776.
- [37] R.R. Gatte, J. Phillips, *Langmuir* 5 (1989) 768.
- [38] J. Phillips, R.R. Gatte, *Thermochim. Acta* 154 (1989) 13.
- [39] R.R. Gatte, J. Phillips, *J. Catal.* 116 (1989) 49.
- [40] R.R. Gatte, J. Phillips, *Thermochim. Acta* 133 (1988) 149.
- [41] R. Wunder, J. Phillips, *J. Phys. Chem.* 98 (1994) 12329.
- [42] R.W. Wunder, J. Phillips, *J. Phys. Chem.* 100 (1996) 14430.
- [43] S.M. da Silva, J. Phillips, *J. Mol. Catal.* 94 (1994) 97.
- [44] J. Phillips, A. Auroux, G. Bergeret, J. Massardier, A. Renouprez, *J. Phys. Chem.* 91 (1993) 3565.
- [45] S.B. Sharma, J.T. Miller, J.A. Dumesic, *J. Catal.* 148 (1994) 198.
- [46] S.B. Sharma, P. Ouraipryvan, H.A. Nair, P. Balaraman, T.W. Root, J.A. Dumesic, *J. Catal.* 150 (1994) 234.
- [47] R.D. Cortright, J.A. Dumesic, *J. Catal.* 148 (1994) 771.
- [48] R.D. Cortright, J.A. Dumesic, *J. Catal.* 157 (1995).
- [49] M.A. Natal-Santiago, S.G. Podkolzin, R.D. Cortright, J.A. Dumesic, submitted to *Catal. Lett.* 1997.
- [50] R.D. Cortright, J.A. Dumesic, *Appl. Catal. A, General* 129 (1995) 101.
- [51] G.D. Borgard, S. Molvik, P. Balaraman, T.W. Root, J.A. Dumesic, *Langmuir* 11 (1995) 2065.
- [52] J. Shen, B.E. Spiewak, J.A. Dumesic, accepted in *Langmuir*, 1997.
- [53] S. Bhatia, F. Engelke, M. Pruski, B.C. Gerstein, T.S. King, *J. Catal.* 147 (1994) 455.
- [54] R.L. Narayan, N. Savargaonkar, M. Pruski, T.S. King, in: J.W. Hightower et al. (Eds.), *11th International Congress on Catalysis – 40th Anniversary*, Vol. 101, Elsevier Science B.V., Amsterdam, 1996.
- [55] J.M. Rojo, J.P. Belzunegui, J. Sanj, J.M. Guil, *J. Phys. Chem.* (1994).
- [56] L. Stradella, *New J. Chem.* 17 (1993) 357.
- [57] S. Cerny, V. Ponec, L. Hládek, *J. Catal.* 5 (1996) 27.
- [58] S. Cerny, M. Smutek, F. Buzek, A. Curínová, *J. Catal.* 47 (1977) 159.
- [59] S. Cerny, M. Smutek, F. Buzek, *J. Catal.* 47 (1977) 166.
- [60] M. Smutek, S. Cerny, *J. Catal.* 47 (1977) 178.
- [61] S. Cerny, M. Smutek, F. Buzek, *J. Catal.* 38 (1975) 245.
- [62] S. Pálfi, W. Lisowski, M. Smutek, S. Cerny, *J. Catal.* 88 (1984) 300.
- [63] O.A. Boeva, K.N. Zhavoronkova, M. Smutek, S. Cerny, *J. Less-Common Met.* 118 (1986) 1.
- [64] S. Cerny, M. Smutek, *J. Catal.* 123 (1990) 275.
- [65] Z. Bastil, S. Cerny, M. Kovár, *Appl. Surf. Sci.* 68 (1993) 275.
- [66] M. Smutek, S. Cerny, *Thermochim. Acta* 91 (1985) 31.
- [67] S. Cerny, *Surf. Sci. Rep.* 26 (1996) 1.
- [68] A. Stuck, C.E. Wartnaby, Y.Y. Yeo, J.T. Stuckless, N. Al-Sarraf, D.A. King, *Surf. Sci.* 349 (1996) 229.
- [69] D.A. King, M.G. Wells, *Surf. Sci.* 29 (1972) 454.
- [70] N. Al-Sarraf, J.T. Stuckless, D.A. King, *Nature* 360 (1992) 243.
- [71] N. Al-Sarraf, J.T. Stuckless, C.E. Wartnaby, D.A. King, *Surf. Sci.* 283 (1993) 427.
- [72] J.T. Stuckless, N. Al-Sarraf, C. Wartnaby, D.A. King, *J. Chem. Phys.* 99 (1993) 2202.
- [73] N. Al-Sarraf, D.A. King, *Surf. Sci.* 1 (1994) 307–309.
- [74] S.J. Dixon-Warren, M. Kovar, C.E. Wartnaby, D.A. King, *Surf. Sci.* 16 (1994) 307–309.
- [75] L. Vattuone, Y.Y. Yeo, D.A. King, *J. Chem. Phys.* 104 (1996) 8096.
- [76] A. Stuck, C.E. Wartnaby, Y.Y. Yeo, D.A. King, *Phys. Rev. Lett.* 74 (1995) 578.
- [77] Y.Y. Yeo, C.E. Wartnaby, D.A. King, *Science* 268 (1995) 1731.
- [78] Y.Y. Yeo, A. Stuck, C.E. Wartnaby, D.A. King, *Chem. Phys. Lett.* 259 (1996) 28.
- [79] Y.Y. Yeo, L. Vattuone, D.A. King, *J. Chem. Phys.* 104 (1996) 3810.
- [80] C.E. Wartnaby, A. Stuck, Y.Y. Yeo, D.A. King, *J. Chem. Phys.* 102 (1995) 1855.
- [81] C.E. Wartnaby, A. Stuck, Y.Y. Yeo, D.A. King, *J. Phys. Chem.* 100 (1996) 12483.
- [82] B.E. Spiewak, J. Shen, J.A. Dumesic, *J. Phys. Chem.* 99 (1995) 17640.
- [83] B.E. Spiewak, P. Levin, R.D. Cortright, J.A. Dumesic, *J. Phys. Chem.* 100 (1996) 17260.
- [84] B.E. Spiewak, B. Fastrup, J.A. Dumesic, in progress, 1997.
- [85] G. Ertl, M. Grunze, M. Weiss, *J. Vac. Technol.* 13 (1976) 314.
- [86] F. Bozso, G. Ertl, M. Grunze, M. Weiss, *J. Catal.* 49 (1977) 18.
- [87] F. Bozso, G. Ertl, M. Weiss, *J. Catal.* 50 (1977) 519.
- [88] B.E. Spiewak, R.D. Cortright, J.A. Dumesic, submitted to *J. Phys. Chem.*, 1997.
- [89] B.E. Spiewak, J.A. Dumesic, unpublished work, 1997.