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NOTE

Microchemisorption

In this note, a new flow chemisorption apparatus is described which is capable of determining catalytically active metal surface areas as small as 0.01 m^2. Also addressed are the serious problems encountered by all researchers measuring small active surface areas on support catalysts. Only in recent literature has the question of detection limits been considered (*1*). In the case of CO chemisorption of a Pt/Al_2O_3 catalyst by flow techniques (*2*), difficulties can be very severe. The uncertain ratio between CO and Pt (*3, 4*), competitive adsorption on the support (*5*), and the presence of weakly bound CO (*6*) can detract seriously from the accurate measurement of metal surface areas. Furthermore, when low Pt loading or small sample sizes must be used, new problems arise because of trace impurities in the carrier gas. If one is attempting to measure 0.01 m^2 of active area (approximately 10^{17} Pt atoms or 1 gm of catalyst containing 0.04% Pt), then 4.6×10^{-3} cc (STP) CO is required to form a monolayer assuming a CO/Pt ratio of one. Restricting a bias to 10% dictates that the total impurities be less than 4.6×10^{-4} cc. The volume of carrier gas typically required to purge and to cool a catalyst after pretreatment can easily be as much as 2400 cc. This is equivalent to an upper limit of impurities of 200 ppb. If one uses UHP research grade He (99.999%) as the carrier gas, impurities are still present at 1000 ppb. Purification is obviously required even though many of the impurities may be innocuous. Even more detrimental to the measurement of low surface areas are leaks caused by joints in conventional equipment.

An *in situ* trap and reversible flow procedure was devised to minimize contamination of carrier gases. Figure 1 shows a schematic of the apparatus with a special three-compartment sample cell and five-port valving system which allows oxygen and moisture traps (Altech Indicating Adsorbent and Kaiser KSA-lite Alumina, respectively) to be placed in immediate proximity to the sample. These traps were regenerated *in situ* by a reverse flow of hydrogen. The sample and traps were initially calcined in air, followed by purging with helium and reduction with hydrogen. While the sample was reduced at 500°C, the oxygen trap was regenerated at 400°C and the moisture trap was dried at approximately 300°C in the cooler section of the trap. When the sample was cooled to room temperature, and the oxygen trap reached 165°C, the gas flow was reversed and switched to helium. Subsequently, all gases entering the tube were scrubbed by the freshly regenerated traps before contacting the sample.

Figure 2 shows the effect of sample size on measured Pt surface area using the chemisorption procedure without the *in situ* traps on a 0.74% Pt/Al_2O_3 catalyst. Despite the use of UHP grade gases, the measured surface area decreased dramatically when sample sizes fell below 50 mg. This effect can be explained by trace impurities in the He carrier gas. Figure 2 also compares the results using our reverse-flow procedure, where essentially constant surface areas were measured down to at least 10 mg sample size. At 10 mg, the active Pt area is 0.017 m^2 if the assumptions are made of a linear CO bonding to each Pt atom with a cross-sectional area of 8.9 Å (*2*). Even with 10-mg samples a standard deviation of only 4% relative was obtained.

Figure 2 seems to indicate a small bias in results between the two procedures. Using a 250-mg sample, where trace poisons are

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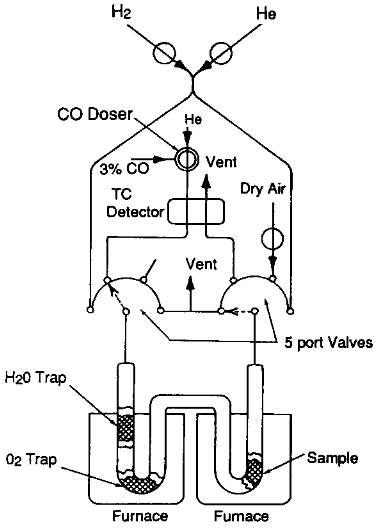

FIG. 1. Microchemisorption apparatus.

not yet important, the conventional procedure gives a 92% dispersion of Pt, whereas the reverse flow procedure indicated 87% dispersion. This discrepancy is likely caused by some minor bias in calculating the blanks. In either case, these data indicate that linear bonding is indeed dominant at this Pt loading.

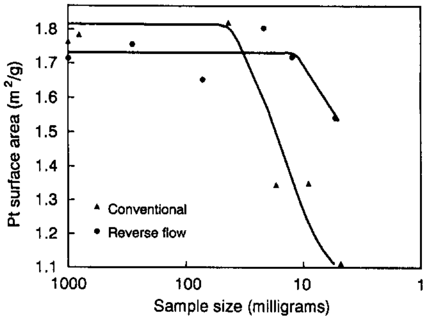

FIG. 2. Pt surface area measured vs sample size.

CO adsorption in the traps was minimized by the conditions and the choice of adsorbents. A Kaiser KSA-lite Alumina activated at 300°C, adequately removed water at room temperature. Under these conditions, only 2.5% of the CO was adsorbed employing a dose of 0.0108 cc CO in 0.36 cc total gas. Oxygen was also suitably removed by the Altech material (Mn on Al_2O_3), activated at 400°C. At 165°C, 1 g of this material adsorbs 1.23% of the above CO pulse.

In conclusion, an improved chemisorption device has been built which has the sensitivity and precision to measure reliably and accurately catalytically active surface areas as small as 0.01 m^2. This high sensitivity permits the analysis of milligram quantities of catalysts with highly dispersed metals or larger samples with poor metal dispersion such as spent catalysts. Other potential applications include single crystal surfaces and evaporated metal films.

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