

Chemisorption of Carbon Monoxide on Metal Surfaces by Pulse Chromatography

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A pulse chromatographic procedure has been developed for the measurement of the surface areas of catalytic metals by carbon monoxide chemisorption. This procedure consists of repeated injection of carbon monoxide pulses into a helium carrier gas passed over the metal surface to establish the cumulative saturation value which corresponds to irreversible chemisorption. Independent measurements made on unsupported platinum and nickel metal powders with volumetric and chromatographic surface area procedures and on supported nickel catalysts with a volumetric chemisorption procedure have established the validity of the pulse chromatographic procedure for determination of carbon monoxide chemisorption. Advantages of the pulse chromatographic procedure include the avoidance of high vacuum procedures and the avoidance of corrections for reversible physical adsorption.

GAS CHEMISORPTION is an established technique commonly used for the estimation of the accessible reactive surface of metal catalysts. The gases most commonly used are hydrogen and carbon monoxide. This technique is applicable to a variety of metal catalysts which include the transition metals (iron, nickel, cobalt, and the platinum family). Volumetric gas adsorption procedures are most commonly used for chemisorption measurement. However, several recent applications have been made of chromatographic procedures (1-6).

Chromatographic measurements have several attractive aspects which include:

1. High vacuum procedures are avoided.
2. Measurements are made under dynamic flow conditions approximating those under which catalysts are most commonly used.

In the present study, a pulse chromatographic procedure has been used to measure the chemisorption of carbon monoxide on supported nickel and unsupported nickel and platinum catalysts. This chemisorption procedure consists of repeated exposure of the catalysts to carbon monoxide pulses to establish the cumulative saturation value which corresponds to irreversible adsorption at room temperature. A comparison is made with results from measurements made with the classical volumetric procedure to establish the equivalence of the gas chemisorption values determined by the two procedures on the

supported nickel catalysts. In the case of the unsupported nickel and platinum catalysts independent measurements of the total surface area by a physical adsorption procedure provide a reference to establish that the chemisorption has occurred over the entire surface of the metal.

The adsorption kinetics for a gas such as carbon monoxide can be expected to vary from one catalytic metal surface to another. Factors which affect the adsorption kinetics include the energy requirements of the adsorbate-metal bond, competition with residual surface impurities, diffusion effects due to fine pore structure, and possible competition of the support material for the given adsorbate. The present procedure is essentially the same as that used by Gruber (1) except that the adsorption kinetics of the metal systems investigated required multiple pulsing to achieve saturation adsorption. The experimental conditions were selected to have the most general applicability for supported and unsupported metal catalysts.

EXPERIMENTAL

Catalysts. Catalysts used in this study included a nickel-on-alumina (Girdler G56-2) 1/4-inch pellets, nickel-on-silica (Girdler G-52) 1/4-inch pellets, nickel on an aluminosilicate (Girdler G60RS) 1/4-inch pellets, and a nickel zeolite (Ni 13XA) 1/8-inch pellets. This nickel zeolite was prepared from Linde 13X by ion exchange of the sodium exchange cations by nickel cations, followed by exhaustive water wash and reduction in hydrogen at 400 °C. Details of the preparation and chemical analyses have been published elsewhere (7). The nickel powder used was a fine particle size obtained from the National Research Corporation, Cambridge, Mass. All the supported catalysts were reduced 16 hours at 350 °C in a stream of hydrogen (0.33 atmos. hydrogen + 0.67 atmos. nitrogen). The nickel powder was reduced in hydrogen at 150 °C to remove surface oxides. The platinum catalyst used was an Engelhard platinum black reduced in hydrogen at 125 °C. Catalyst samples were purged at 100 °C with the helium carrier gas for at least an hour after hydrogen reduction and before the carbon monoxide pulse adsorption measurements.

Gas Preparation. The carbon monoxide used was of high purity (99.5%), obtained from the Matheson Co., Inc., East Rutherford, N. J. This gas was purified further by passing over active platinum black at 300 °C and dried over a molecular sieve adsorbent bed.

Chemical Analyses. The nickel content of the nickel catalysts was determined by a standard wet procedure (dimethyl glyoxime precipitation).

Apparatus. The chromatographic apparatus used was a modified Shell-Perkin-Elmer Sorptometer (8). A schematic

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- (1) Hans L. Gruber, *ANAL. CHEM.*, **13**, 1828 (1962).
- (2) T. R. Hughes, R. J. Houston, and R. P. Sieg, *Ind. Eng. Chem., Process, Des. Develop.*, **1**, 96 (1962).
- (3) N. E. Buyanova, A. P. Karanaukhov, L. M. Kefeli, F. D. Ratner, and O. N. Chernyavskaya, *Kinetics Catalysis*, **8**, 737 (1967).
- (4) O. Piringer and E. Tataru, *J. Gas Chromatogr.*, **2**, 323 (1964).
- (5) P. Fejes, F. Nagy, and G. Schay, *Acta Chim. Acad. Sci. Hung.*, **20**, 451 (1958).
- (6) F. F. Roca, L. de Mourgues, and Y. Trambouze, *J. Gas Chromatogr.*, **6**, 161 (1968).

- (7) C. S. Brooks and G. L. M. Christopher, Abstracts I-54, 154th National Meeting, ACS, September 1967; *J. Catal.*, **10**, 211 (1968).
- (8) Shell-Perkin-Elmer Sorptometer (Model 212) Instruction Manual. Instrument Division, Perkin-Elmer, Norwalk, Conn. (Oct. 1960).

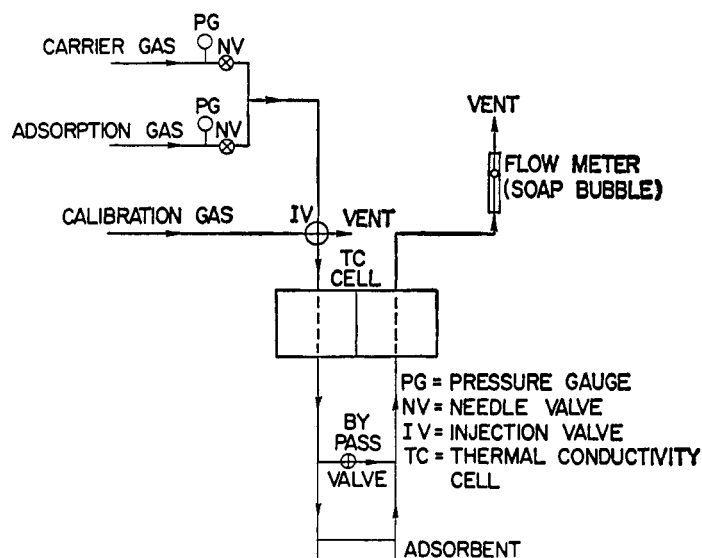


Figure 1. Schematic diagram of continuous flow adsorption apparatus

diagram of the apparatus and adsorbent mounting is shown in Figure 1. The catalyst samples were mounted in borosilicate glass U-tubes (0.6 cm i.d. \times 10 cm.). Description of the basic instrument is sufficiently complete in Reference 8 that no further details are presented here. The response of the thermistor detector was linear for the range of carbon monoxide concentrations used. The principal modification consisted of relocating the calibration valve (IV), which consists of U-tubes with calibrated volumes varying from 0.5 to 3 ml in size, upstream from the first chamber of the thermistor detector. The calibrated volumes used for the present experiments were 1.475 cm³ for nickel catalysts and 1.421 cm³ for the platinum catalysts.

Chromatographic Procedure. In the pulse chromatographic procedure the peak area corresponding to a pulse of carbon monoxide in a helium carrier gas (50 cm³ STP/min) passed over a catalyst sample is measured before and after contact with the catalyst. The observed decrease in the carbon monoxide peak area is attributed to irreversible retention of chemisorbed carbon monoxide on the catalyst. The calibration valve was used to inject the carbon monoxide into the helium elution stream immediately upstream from the first chamber of the thermistor detector. The catalyst sample tube was mounted in the helium flow stream so that the injected carbon monoxide pulse passed over the catalyst before entering the second chamber of the thermistor detector.

Catalyst sample weights ranged from 0.1 gram for the high surface area zeolites to 0.25 gram for the low surface area metal blacks. This means that each carbon monoxide pulse (\sim 1.4 cm³) used in the present experiments corresponded to \sim 0.5 to 2 monomolecular adsorbate layers, depending upon whether the adsorbent was a zeolite or a metal powder. It is desirable to select a pulse size that is about one to two monomolecular adsorbate layers for a given sample so that each increment of adsorption represents an appreciable fraction of a given carbon monoxide pulse. The pelleted catalysts were usually used without crushing. No difference in adsorption was observed for the pelleted catalysts when crushed.

It is essential that there be no appreciable change in the helium flow rate due to a pressure drop through the catalyst bed in order to maintain the same time base for the peak areas before and after contact with the catalyst. A difference in carbon monoxide peak areas may be observed between the first and second detector chamber due to a decrease in carrier gas flow rate. In order to correct for this, calibration pulses can be sent to the second detector chamber with the catalyst

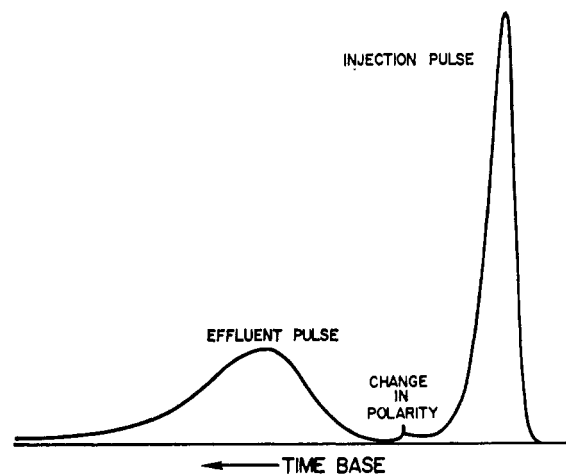


Figure 2. Carbon monoxide chemisorption on a nickel catalyst at room temperature by a pulse chromatographic procedure

holder on bypass and the reference peak area used is then either the average of the first and second peak areas (with the catalyst holder on bypass) or the second peak area. Differences in the first and second peak areas of the order of 8% have been observed, but the above indicated correction procedures can reduce this to no more than 1%.

The peak areas are integrated and the equivalence of chart area to gas volume is established by the injection of known volumes of carbon monoxide into the helium flow stream passed through the empty catalyst holder or to the second detector chamber with the catalyst holder on bypass. Typical signal traces are shown in Figure 2. A minimum carrier flow rate of 50 cm³ per minute is necessary to minimize tailing and prevent excessive error in the peak area integration.

Experiments were performed with carbon monoxide at temperatures of -78 and 23 $^{\circ}\text{C}$, because these are conveniently maintainable temperatures which provide an appreciable interval above the normal boiling point of carbon monoxide.

RESULTS AND DISCUSSION

Both frontal and pulse chromatographic procedures were examined. In frontal analysis the adsorbate gas is injected into the helium carrier gas until a given partial pressure is attained. This partial pressure is maintained for an interval of several minutes, then the adsorbate gas is discontinued to permit the initial helium carrier gas composition to be re-established. In this procedure the signal traces for the sample tube empty and for the adsorbent present with the starting times matched are superimposed and the amount of adsorbed gas is calculated from the area enclosed between the signal traces at the leading edge during the establishment of the adsorbate plateau of constant partial pressure. The amount of desorbed gas is obtained in a similar fashion from the tailing edge of the plateau where the adsorbate signal trace is declining from the plateau of constant partial pressure to the helium base line free of adsorbate. This technique has been used with some success for the measurement of the physical adsorption of water and organic vapors on minerals at moderate temperatures (9). The pulse procedure was found more applicable for chemisorption.

The results of exposure of several catalysts to successive carbon monoxide pulses at room temperature are presented in

(9) C. S. Brooks, *Soil Sci.*, **99**, 182 (1965).

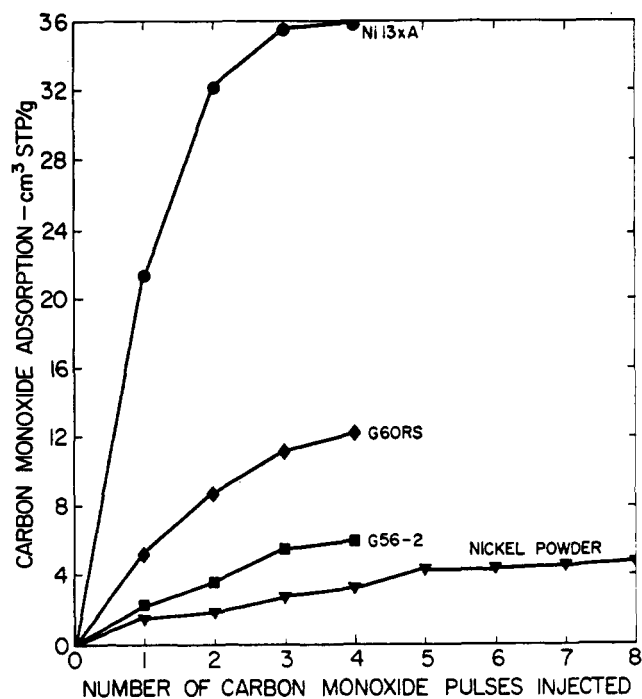


Figure 3. Chemisorption of carbon monoxide on nickel surfaces at room temperature by a pulse chromatographic procedure

Figure 3. The catalysts included a nickel powder, a nickel zeolite (Ni 13XA), nickel on alumino-silicate with zirconium promoter (Girdler G-60RS), and nickel-on-alumina (Girdler G56-2). The results of similar measurements on a platinum catalyst (Engelhard black) at -78°C are presented in Figure 4.

There is a reversible physical adsorption component which complicates selection of the most suitable experimental conditions for establishing the irreversible chemisorption component. Rideal and Trapnell (10) found that a portion of the carbon monoxide adsorbed on nickel around room temperature has a heat of adsorption as low as 4 kcal/mole and of the magnitude to be expected for purely physical adsorption.

A somewhat sharper differentiation might be made between the reversible physical adsorption component and the irreversible chemisorption component by employing a lower temperature, such as -78°C . However, the disadvantage of using the lower temperature compared with room temperature is that the physical adsorption of carbon monoxide on supports such as the zeolites becomes a much more significant fraction of the total observed adsorption. The magnitude of any irreversible carbon monoxide adsorption on the catalyst supports or promoters should be established by making separate measurements by the same procedure with the support alone. A decided advantage of the pulse chromatographic procedure over the volumetric procedure is that correction for reversible physical adsorption on support or promoters is unnecessary.

In a nonequilibrium adsorption procedure such as described here, several factors may contribute to the slow equilibration rate which requires exposure to multiple carbon monoxide pulses to attain a saturation adsorption value. Three possible factors can be suggested:

1. A slow reorientation of the adsorbed carbon monoxide from an initial bridged to a final linear configuration.

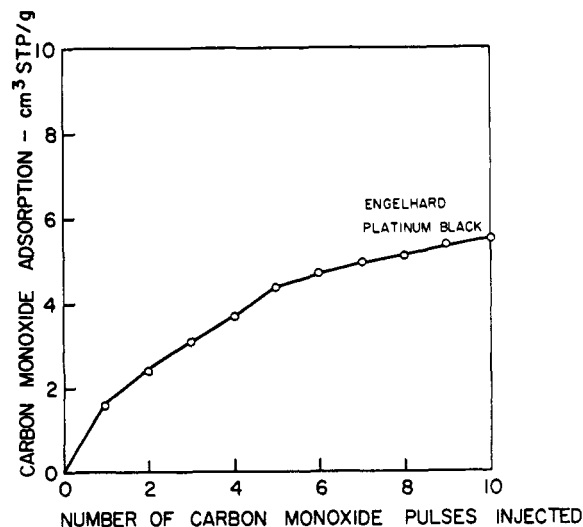


Figure 4. Chemisorption of carbon monoxide on platinum surfaces at -78°C by a pulse chromatographic procedure

2. Competition for adsorption sites with residual hydrogen from reduction.
3. Diffusion effects due to fine pore structure, notably in the case of nickel supported on zeolite (Ni 13XA).

The mild purging conditions used after hydrogen reduction and prior to the carbon monoxide pulse adsorption may very well leave some hydrogen adsorbed on the metal catalyst surfaces. This would result in some competitive adsorption occurring upon contact with the carbon monoxide pulses and may in part account for the necessity of using repetitive pulsing to achieve the saturation carbon monoxide adsorption value. Preheating the supported catalysts can be used to desorb residual adsorbed hydrogen prior to carbon monoxide adsorption, but this is not advisable for unsupported metal blacks such as platinum and nickel which readily sinter in the presence of hydrogen.

The reproducibility of the saturation adsorption values on duplicate portions of a given catalyst sample is of the order of 15%. A repetition of the carbon monoxide adsorption measurements on a given sample portion is not feasible, for these catalysts saturated with adsorbed carbon monoxide can not be heated to desorb the carbon monoxide without sintering the metal or volatilizing the metal as a metal carbonyl.

Confirmation that the pulse chromatographic procedure provides a measure of irreversible carbon monoxide chemisorption on supported nickel catalysts is provided by comparison with values obtained by a conventional volumetric procedure (7). The volumetric data were obtained by equilibration at 400–600 mm Hg vapor pressure and desorption to 50 mm Hg vapor pressure. The carbon monoxide chemisorption values on nickel zeolite were corrected by subtracting the value obtained for the support alone to obtain the irreversible chemisorption on the nickel at a temperature of 23°C and carbon monoxide vapor pressure of 100 mm of Hg. It is evident from the results shown in Table I that the dynamic chromatographic procedure and the equilibrium volumetric procedure lead to results which agree within 20% for the carbon monoxide chemisorbed on nickel at room temperature. It is also evident that at least eight pulses are required to ensure the establishment of the saturation irreversible chemisorption. A larger number of pulses should be used as necessary to ensure a saturation carbon monoxide adsorption.

(10) E. K. Rideal and B. M. W. Trapnell, *Proc. Roy. Soc., Ser. A* 205, 409 (1951).

Table I. Comparison of Carbon Monoxide Adsorption Capacity of Metal Catalysts Measured by Chromatographic and Volumetric Procedures

Adsorbent	Nickel content wt. %	Carbon monoxide adsorption cm ³ STP/q				Volumetric procedure 100 mm Hg V.P. corrected for support
		Chromatographic procedure			Total	
		4 Pulses	8 Pulses	10 Pulses		
Nickel powder	100	3.3	4.9		3.5	
Nickel zeolite (Ni 13XA)	6.68	36.2			36	34
Siliceous support with CaO promoter (Girdler G52)	32	17.0			14.4	
Aluminosilicate support with zirconium promoter (Girdler G60RS)	35	12.2			13.2	
Nickel-on-alumina (Girdler G56-2)	13.1	5.7			4.5	
Platinum powder	100	3.7	5.2	5.6	...	

Additional confirmation is provided by a comparison of the surface areas estimated by the irreversible chemisorption of carbon monoxide at room temperature on nickel and at -78°C on platinum by the chromatographic procedure with surface areas determined by low temperature physical adsorption of nitrogen at -196°C .

The nickel area was estimated from the relationship

$$A \text{ m}^2/\text{g} = \frac{VN\sigma}{2.24 \times 10^8}$$

where V is the volume of adsorbate in cm³ STP/g, N is Avogadro's number, and σ is the effective molecular coverage area of the molecule in an adsorbed monomolecular layer. The nickel powder area was calculated to be 17 or 21 m²/g, respectively, depending upon whether 13×10^{-16} cm²/molecule or 16×10^{-16} cm²/molecule is used for σ . The platinum black area was calculated to be 19 m²/g or 24 m²/g, respectively, de-

pending upon whether 13×10^{-16} cm²/molecule or 16×10^{-16} cm²/molecule is used for σ . The former value is the value most commonly used in the literature for chemisorbed carbon monoxide (11), whereas the latter value corresponds to the physically adsorbed carbon monoxide adsorbate molecule (12). In either case the area estimated from carbon monoxide adsorption agrees within 5 to 20% with the surface areas of 22 m²/g for nickel and 20 m²/g for platinum calculated from the low temperature nitrogen adsorption measurements at -196°C employing the BET equation (13).

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- (11) R. J. Kokes and P. H. Emmett, *J. Amer. Chem. Soc.*, **82**, 1037 (1960).
- (12) H. K. Livingston, *J. Colloid Sci.*, **4**, 450 (1949).
- (13) P. H. Emmett and S. Brunauer, *J. Amer. Chem. Soc.*, **59**, 1553 (1937).