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Chemisorption on Molecular Sieve Supported Platinum

II. Carbon Monoxide

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Studies have been made of the measurement of metal surface areas of platinum catalysts supported on molecular sieve, using a gas chromatographic pulse technique and thermodesorption. It has been found possible to identify conditions where carbon monoxide chemisorbs on platinum and not on the support. The values of metal surface areas measured under these conditions agree well with metal surface areas determined by chemisorption of hydrogen and of oxygen and by direct electron microscopic examination. The results indicate that 0.55 molecules of carbon monoxide are adsorbed per platinum surface atom, a value that suggests the gas is mainly bridge-bonded under the conditions of measurement.

INTRODUCTION

The measurement of metal surface areas of supported metal catalysts by the adsorption of carbon monoxide poses several difficulties. Although carbon monoxide is usually adsorbed selectively by the metal, it is well known that both one and two site adsorption can occur (*1–4*), the gas being adsorbed either in a linear (CO:metal = 1) or a bridged (CO:metal = 0.5) form. As a further complication, Gruber (*4*) has established that the percentage of bridged carbon monoxide is a function of metal dispersion, a fact confirmed by Dorling and Moss (*5*).

The determination of metal surface areas of newer types of reforming catalyst can also be difficult. Where the metal is supported on a molecular sieve, carbon monoxide can adsorb on the supported metal as well as on the support (*6*). The present studies have been concerned with the measurement of metal areas in such systems, using a 0.3% Pt on molecular sieve 5A catalyst which had been well characterized in a previous study (*7*). The previous work involved the characterization of the catalyst by electron microscopic examination, by chemisorption of hydrogen and oxygen and by hydrogen–oxygen titration. Attention was paid to the pretreatment procedure necessary to clean the catalyst: this involves reduction with hydrogen followed by careful degassing (*7*).

Cleanliness of the metal surface is also required when the surface reaction between chemisorbed oxygen and carbon monoxide is used to measure the platinum surface area (*8*). Choice of carbon monoxide for adsorption was made to avoid at least part of this problem, in that hydrogen has been reported not to interfere with the chemisorption of CO (*9, 10*).

The adsorption of CO on platinum has been studied by many workers (*11–14*). The objective of the present work was to develop a practical method for measuring surface area and no assumption was made as to the type of carbon monoxide–platinum bonding. An indication of the results

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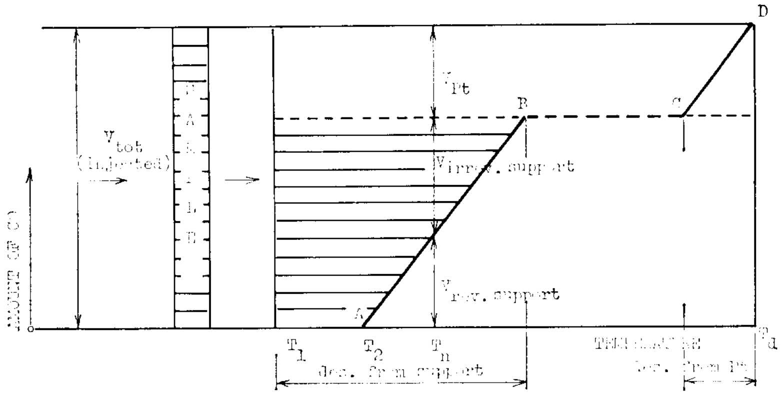

FIG. 1. Scheme for location of the experimental temperature for measurement of the specific surface of platinum in Pt-molecular sieve material by CO chemisorption.

to be expected can be obtained from the work of Hightower and Emmett (*15*) who found that one molecule of chemisorbed carbon monoxide covers 16.2 Å^2 of platinum surface, which recalculated gives CO/Pt$_{surf}$ = 0.55.

EXPERIMENTAL METHODS

The experimental equipment and procedure has been described previously (*7*). The most significant change was in the pretreatment procedure where more severe reduction conditions were applied. The sample for carbon monoxide measurements was usually exposed to 100 ml H_2/min, at 485°C for about 14 hr, in order to obtain a stable state of platinum crystallites within the range of experimental conditions applied. A pulse technique was used and the amount of carbon monoxide in the pulse was in excess of that needed to saturate the sample. Calibration of the catharometer for CO was made for every experiment. After the chemisorption measurement was carried out, carbon monoxide was desorbed from platinum by thermodesorption.

RESULTS AND DISCUSSION

Carbon monoxide was found to adsorb both on platinum and in molecular sieves at room temperature, and attention was directed at establishing conditions where desorption from the support was favored while gas remained adsorbed on the metal.

The theoretical basis of the approach can be discussed with the aid of Fig. 1. In this model, the strength of adsorption

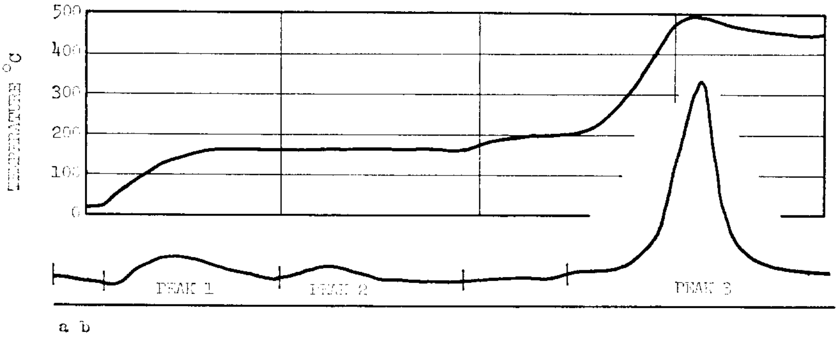

FIG. 2. Profile of thermodesorption of carbon monoxide adsorbed at room temperature on 5A-0.3.

TABLE 1

Chemisorption of Carbon Monoxide on 1.8986 g of 0.3% Pt-Molec. Sieve 5A

Temp (°C)	Amount of CO (μl)		
	Injected	Retained (CO diff.)	Thermodes. (485°C)
300	105	52	33
325	109	49	23
350	85	40	—[a]
375	93	38	8
275	255	68	41
250	222	86	49

[a] After the carrier gas was flushed over the catalyst overnight the thermodesorption up to 485°C gave 3.5 μl CO.

is assumed to vary linearly with coverage and irreversible adsorption is taken to be that gas which is not eluted within 12.5 min (*16*). For injection of the same amount of CO, the fraction of reversibly adsorbed gas V_{rev} will increase with temperature along the line AB ($T_n > T_2 > T_1$) until the point where all the gas adsorbed on the carrier can be desorbed. As the temperature is increased still further, desorption from the metal starts to be important (C). Of course, in a real system, continuous variation of adsorption strengths is unlikely, and this model is only descriptive.

Initial experiments carried out at room temperature showed that adsorption of carbon monoxide occurred on both the metal and the carrier. The emergent pulse was spread over some 35 min, with a peak at a retention time of 22 min: at least some gas was retained. The temperature of the catalyst was then increased slowly, and the desorbed gas recorded as a function of temperature (Fig. 2). The existence of adsorbed gas with differing heats of adsorption is clearly seen. After emergence of the tail of the room temperature desorption (Fig. 2, ab), a small peak emerged at about 100°C. The temperature was then held constant at 170°C for 8 min, when a second peak (Fig. 2, peak 2) emerged. The temperature was then increased to 485°C in slow stages: during this increase, a major peak was found to develop (peak 3).

A sample of molecular sieve 5A was then treated with ammonium chloride under the same conditions as the catalyst was normally prepared from platinum ammonia chloride complex [$Pt(NH_3)_6Cl_4$] and used in the adsorption rig. Two strongly adsorbed forms of carbon monoxide were observed, desorption of the strongest (ca. 3% of the total) being complete by ca. 200°C.

As a result of this finding, CO adsorption on the catalyst was studied at temperatures greater than 200°C by passing pulses of gas over the catalyst at various adsorption temperatures. The difference between injected and eluted carbon monoxide was recorded as retained volume (Table 1). The catalyst was then heated rapidly to 485°C and the amount of gas desorbed recorded (thermodesorbed volume). The results are summarized in Table 1.

Full saturation of the catalyst by CO at 300°C was shown by the fact that changes in injected volume had little effect on the total volume retained (Table 1). The recoverable gas volume was found to decrease with increasing temperature, with the thermodesorbed volume always being

TABLE 2

Chemisorption of Carbon Monoxide on 1.8920 g of 0.3% Pt-Molec. Sieve 5A

Temp (°C)	Amount of CO (μl)		
	Injected	Retained (CO diff.)	Thermodes. (485°C)
175	206	97	78
200	316	89.5	69.5
200	133	96	69
200	263	85	72
220	241	80	72
225	169	84	61

less than the retained volume. Sequential measurement of adsorbed gas at low temperatures, high temperatures and low temperatures showed that blocking of the surface (for example, by carbon formation) could occur, but was not responsible for more than 2% of the observed difference except at higher temperatures.

As a result of this finding, attention was directed at adsorption at lower temperatures and the possibility of using the gas emerging as peak 2 (Fig. 2) was explored. Detailed results of experiments carried out with the reactor maintained near to 200°C are reported in Table 2. It is seen that the retained volume is always greater than the thermodesorbed volume, but that the latter is remarkably constant for adsorption temperatures in the range 200–220°C. Adsorption at 175°C is almost certainly affected by adsorption on the support, and it is suspected that tailing in the peaks used to calculate the retained volume results from the same cause. As a consequence, thermodesorbed volumes were used to calculate the ratio of CO adsorbed to total platinum (Table 3). The values were found to be between 0.105 and 0.110.

Previous studies of the catalyst using electron microscopy have shown that the platinum crystallites have a mean diameter of 46 Å, giving a ratio of Pt_{surf}/Pt_{tot} of 0.2 ± 0.02 depending on the geometry assumed (*7*). On this basis, the CO/Pt_{surf} ratio is found to be 0.53 ± 0.02, in good agreement with the value of 0.55 reported by Hightower and Emmett (*15*).

Liquid CO has a density of 0.793 g/ml and one molecule of the liquid will occupy 58.6 Å^3. Assuming a cube, this means that the area covered by one molecule is 15.1 Å^2. Now the present measurements show that there are 0.55 molecules of CO/Pt which gives an area covered per molecule of $0.55 \times 15.1 = 8.5$ Å^2, a value to compare with the surface area of a Pt of 8.9 Å^2. This is interesting to note, although this calculation is approximate, since the adsorbed gas will be closer packed than a liquid. The value obtained ($CO/Pt_{surf} = 0.55$) is in reasonable agreement with carbon monoxide adsorbed on 2 Pt atoms in crystallites in which the stoichiometry may be different at the edges and corners (*1*, *17*).

TABLE 3

Adsorption Ratios Giving a Measure of the Platinum Surface Area[a]

Temp (°C)	CO/Pt_{tot}	$Adsorbate/Pt_{tot}$
200	0.106	0.193
200	0.105	0.192
200	0.110	0.200
220	0.110	0.200

[a] From Table 2. CO/Pt_{tot} calcd on the basis of CO adsorbed on total platinum as measured by thermodesorption. $Adsorbate/Pt_{tot}$ calcd from the CO adsorption results, but on the basis of 1 adsorbate molecule/surface Pt molecule and assuming $CO/Pt_{surf} = 0.55$.

Using the ratio of CO/Pt_{surf} of 0.55, the ratios of $adsorbate/Pt_{tot}$ were calculated (Table 3) from the CO/Pt_{tot} value on the basis of a stoichiometry of one adsorbate molecule per one surface Pt molecule. These are comparable with values of O/Pt_{tot} and H/Pt_{tot} measured experimentally on the same catalyst in which the stoichiometry is one (*7*). The agreement recorded (CO adsorption and the $CO/Pt_{surf} = 0.55$ model gives 0.196 ± 0.004; O_2 adsorption gives 0.17 ± 0.02; H_2 adsorption gives 0.17 ± 0.01) supports the contention that the method developed gives a measure only of the metal surface area.

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