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Thermodynamics of Sulfur Chemisorption on Metals

IV. Alumina-Supported Platinum

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Isosteric heats of chemisorption of sulfur on alumina-supported platinum catalysts have been determined as a function of surface coverage resulting from exposure to H_2S/H_2 gas mixtures. At low coverage the heat of chemisorption with reference to $\frac{1}{2}$ S_2(g) is -208 ± 11 kJ · mol^{-1}. The heat of chemisorption decreases to -177 kJ · mol^{-1} at half saturation coverage. Except at very low coverage, the thermodynamic activity of sulfur chemisorbed on platinum is greater than that of iron, nickel, cobalt, and ruthenium.

INTRODUCTION

The adsorption of sulfur on platinum surfaces is an important industrial problem as manifested, for example, in the poisoning of hydrocarbon reforming catalysts (*1*). To overcome this problem, extensive sulfur removal processes must be installed upstream of the reformer. In some cases, however, low surface coverage with sulfur has been found to enhance the selectivity for a particular product (*2*) with some loss in conversion rate. In the measurements to be described, we have examined the reversible thermodynamics of the S/Pt adsorption system. Isosteric heats of sulfur chemisorption on alumina-supported platinum have been evaluated by means of an experimental technique previously applied to sulfur chemisorption studies for Ni (*3*), Ru (*4*), Fe, and Co (*5*).

On an atomic scale, the structure of sulfur adlayers has been investigated for several single crystal planes of platinum. Berthier *et al.* (*6, 7*) used low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and radiotracer techniques to investigate the structure of sulfur adsorbed in the (100), (111), and (110) planes of Pt. Bonzel and Ku (*8, 9*) used LEED and AES to examine sulfur adsorption on Pt (110). Heegemann *et al.* (*10*) used LEED, AES, and thermal desorption to investigate sulfur adsorption on Pt(100) and Pt(111). In the latter study the adsorbing gas was S_2, whereas H_2S was used in all previous studies. Fischer and Kelemen (*11*) used LEED, AES, and ultraviolet photoemission spectroscopy (UPS) to examine the structure and properties of Pt(100). All studies were in reasonable good agreement. On Pt(100), increasing sulfur exposure at room temperature gives, successively, a $p(2 \times 2)$ structure at 3×10^{14} atoms/cm^2, a $c(2 \times 2)$ structure at 6.5×10^{14} atoms/cm^2, and two disordered overlayer structures (*10*) for coverage to 14.5×10^{14} atoms/cm^2 observed with S_2 exposure. On Pt(111), increasing sulfur exposure gives, in order, a $p(2 \times 2)$ structure at 4×10^{14} atoms/cm^2, a $\sqrt{3} \times \sqrt{3}$ R 30° structure at 5×10^{14} atoms/cm^2, a complex hexagonal pattern at 6×10^{14} atoms/cm^2, and disordered overlayers for S_2 exposure to 14×10^{14} atoms/cm^2. On Pt(110), increased H_2S exposure (*6*) gave a series of centered coincidence mesh structures with patterns from $c(2 \times 6)$ through $p(4 \times 4)$ for coverage from 3 to 7×10^{14} atoms/cm^2. These patterns apparently arise

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from the periodic arrangement of vacancies (*7*) in a dense sulfur adlayer with nearly 1 sulfur atom per (100) site.

In general, the formation of a periodic two-dimensional sulfur adlayer on platinum surfaces leads to a severe catalytic deactivation. Bonzel and Ku (*9*) have shown on Pt(110) that for $\theta_s > 0.28$ monolayer, oxidation of CO virtually ceases, presumably because of the inability of the ordered layer to dissociatively adsorb O_2. Fisher and Kelemen (*12*) have observed that catalytic reactions such as dissociative adsorption of H_2S, reduction of NO by CO, the dissociative adsorption of NO, and the adsorption and dehydrogenation of benzene and acetylene are all severely reduced when the sulfur coverage reaches one-quarter monolayer ($\theta_s = 0.25$). This coverage with sulfur corresponds to the coverage of the $p(2 \times 2)$ structure. Adsorption is affected, but not prohibited, by the formation of the $p(2 \times 2)$ structure, but Langmuir–Hinshelwood reactions are prevented. Chemisorption ceases at half monolayer $\theta_s = 0.5$) corresponding to the $c(2 \times 2)$ sulfur adlayer. Presumably, the activity and selectivity of reactions catalyzed by Pt are most significantly altered for sulfur coverage near $\theta_s = 0.25$, or approximately half saturation coverage. Therefore, thermodynamic data for reversible sulfur chemisorption on Pt surfaces are most important for sulfur coverages close to half saturation.

The objective of the present investigation is a quantitative study of the thermodynamics of sulfur chemisorption on alumina-supported platinum catalysts. Such measurements are most valuable for sulfur coverage of less than 5×10^{14} atoms/cm^2, in which the most significant changes in the catalytic properties of platinum occur.

EXPERIMENTAL METHODS

The experimental method used in our study of sulfur chemisorption isosteres has been previously described in detail (*3*, *4*). In the present study, the quartz reactor formerly used in the closed gas-recirculation system was replaced by a flow-through reactor (shown in Fig. 1). The new design provided two advantages: (1) less resistance to gas flow to and from the recirculating gas pump, and (2) magnetic valves that could be raised during gas sampling and lowered to isolate the catalyst during high temperature treatment to uniformly distribute sulfur on surface sites. The volume of the microreactor was about 5 ml and that of the recirculating system about 300 ml.

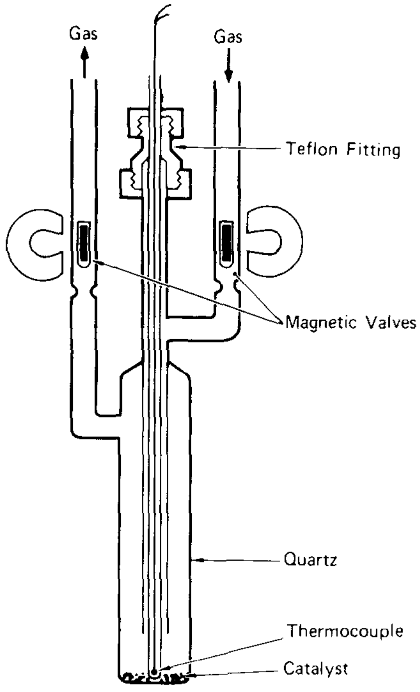

FIG. 1. Quartz microreactor.

A sample of powdered catalyst ($<20 \times 10^{-3}$ g) was placed in the quartz microreactor through which hydrogen (1 atm) was recirculated. The catalyst was reduced by raising the temperature in steps (475 K, 10 min; 625 K, 10 min; 775 K, 10 min; 1025 K, 18 h). During an experiment, aliquots (0.36 cm^3) of H_2S (0.31 vol% in He) were injected into the closed loop and H_2S concentration in the recirculating gas was analyzed with a calibrated photoionization detector. For uniform distribution of the sulfur on the catalyst surface, the H_2S was first adsorbed on the catalyst at a relatively low temperature

(700 K), and then the temperature of the catalyst was raised (800 to 1000 K) after the microreactor was isolated by closing the magnetic valves. Once the sulfur coverage had become uniform, isosteres were measured by varying the sample temperature and monitoring the H_2S partial pressure in the recirculating gas (magnetic valves open). Isosteres were determined in descending and ascending temperatures sequences. Note that, at the H_2S concentration levels typically measured in the recirculating gas (<1 ppm), the amount of sulfur in the loop was significantly less than 1 vol% of the amount of chemisorbed sulfur.

TABLE 1

Sulfur Chemisorption Isosteres for Pt/Al_2O_3 (5.0 wt%) (Least Squares Analysis)

ξ_s[a] coverage	Run no.	ΔH_{ads} ($kJ \cdot mol^{-1}$)	ΔS_{ads} ($J \cdot mol^{-1} \cdot K^{-1}$)	r[b]	n[c]
0.11	I	−119 ± 11	21 ± 12	0.996	15
0.17	I	−103 ± 7	23 ± 8	0.998	17
0.23	I	−93 ± 5	21 ± 6	0.990	29
0.23	II	−88 ± 5	25 ± 5	0.998	14
0.29	I	−88 ± 4	10 ± 5	0.999	15
0.40	II	−67 ± 5	25 ± 7	0.998	19
0.46	II	−47 ± 2	37 ± 5	0.999	15
0.57	II	−27 ± 4	63 ± 8	0.990	19
0.69	II	−34 ± 8	46 ± 17	0.973	16

[a] Sulfur adsorption normalized to CO adsorption at 300 K.
[b] r = least squares correlation coefficient.
[c] n = number of data points.

The Pt sample used for the sulfur chemisorption studies consisted of 5 wt% platinum on an α-alumina support (Kaiser, 20 $m^2 \cdot g^{-1}$ and <250 mesh). The catalyst was prepared by impregnating a sample of the alumina (previously calcined in oxygen at 1120 K) to incipient wetness with an aqueous solution of chloroplatinic acid, drying at 320 K, then calcinating at 625 K for 2 h with 1 vol% O_2 in He flowing over the catalyst. The adsorption capacity of the prereduced catalyst (see procedure above) was measured by CO adsorption at 300 K and found to be 23.1×10^{-6} mol CO per g catalyst, which is equivalent to a Pt surface area of 26.0 $m^2 \cdot g^{-1}$ Pt. The Pt dispersion of the catalyst was quite low since we wanted to compare our adsorption results with measurements made on single-crystal surfaces. In addition, we selected an α-alumina support of low surface area to minimize the

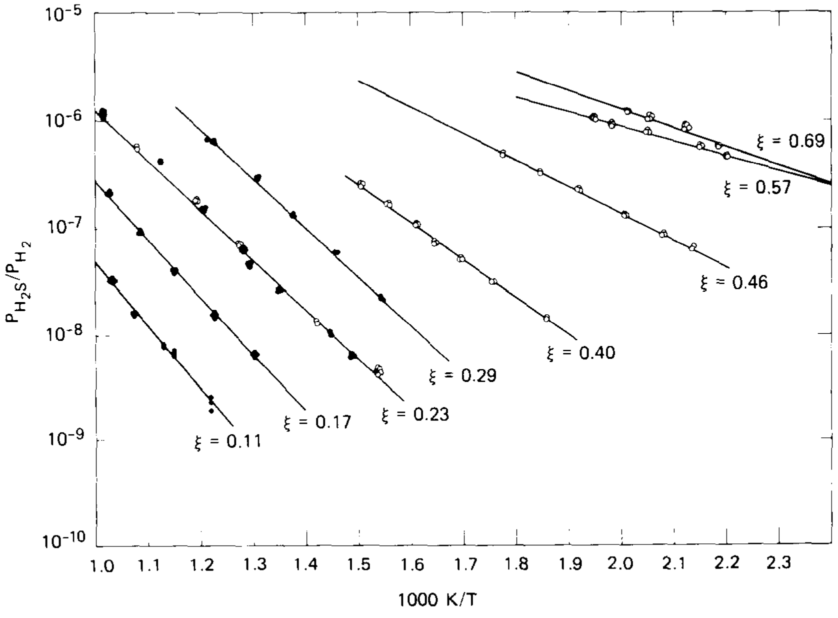

FIG. 2. Chemisorption isosteres of sulfur on 5.0 wt% $Pt/Al_2/O_3$. Fractional surface coverage ξ normalized to CO adsorption at 300 K. ● Run I; ○ run II.

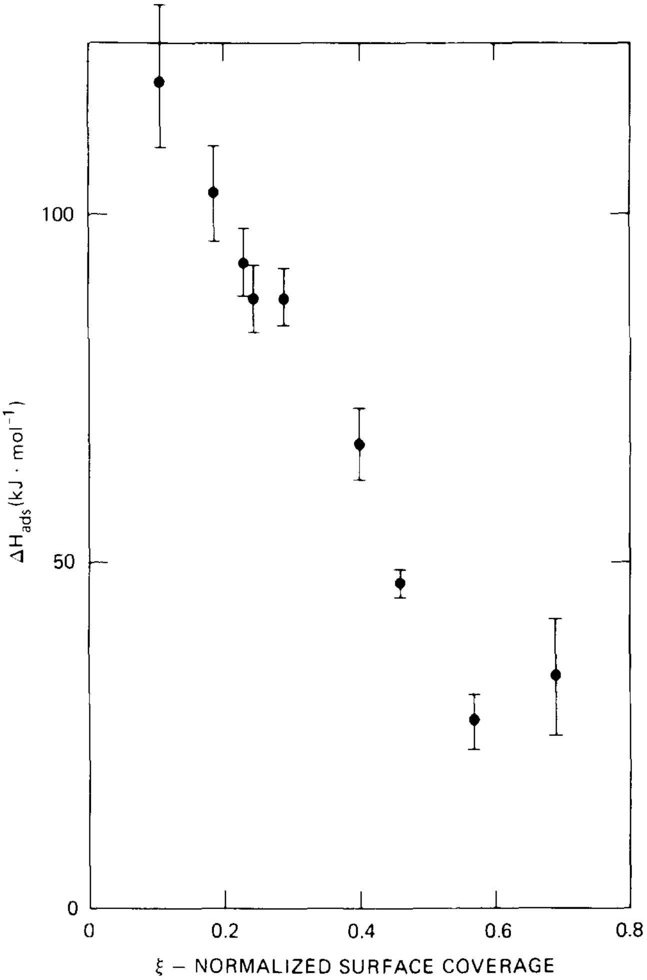

FIG. 3. Heat of adsorption of sulfur on $Pt/Al_2/O_3$ versus fractional surface coverage. ξ normalized to CO adsorption at 300 K.

contribution of H_2S adsorption on the support (*3*).

RESULTS

The chemisorption isosteres on Pt/Al_2O_3 were determined by measuring the thermodynamic activity of gaseous sulfur (expressed as the fraction P_{H_2S}/P_{H_2S}) as a function of temperature for several values of sulfur coverage (Fig. 2). Two runs (I and II) were made on separate samples of the catalyst. The enthalpy and entropy for sulfur adsorption given by the reaction, $H_2S(g) \rightleftarrows S(a) + H_2(g)$, were calculated from a least-squares analysis of the logarithm of sulfur activity versus reciprocal temperature (Table 1, Fig. 3). The sulfur coverage ξ_s is the amount of adsorbed sulfur normalized to the average platinum site density, which was determined by CO adsorption to saturation coverage at 300 K.

The standard enthalpies and entropies of formation for sulfur adsorbed [S(a)] on Pt/Al_2O_3 (Table 2) were determined from the isosteric adsorption data and the tabulated thermodynamic properties of H_2S and H_2 with $\frac{1}{2}$ $S_2(g)$ as the reference state, as described previously (*4*).

TABLE 2

Enthalpy and Entropy of Formation for Sulfur Chemisorption on Pt/Al_2O_3 (5.0 wt.%)

ξ_s[a] coverage	Run no.	$\Delta H_f^{\circ b}$ ($kJ \cdot mol^{-1}$)	$S_f^{\circ b}$ ($J \cdot mol^{-1} \cdot K^{-1}$)	T_{avg} (K)
0.11	I	−208 ± 11	106 ± 12	898
0.17	I	−192 ± 7	108 ± 8	855
0.23	I	−182 ± 5	104 ± 6	800
0.23	II	−176 ± 5	104 ± 5	800
0.29	I	−177 ± 4	92 ± 5	733
0.40	II	−155 ± 5	105 ± 7	607
0.46	II	−134 ± 2	116 ± 5	508
0.57	II	−133 ± 3	141 ± 8	487
0.69	II	−120 ± 8	124 ± 17	478

[a] Sulfur coverage normalized to CO adsorption at 300 K.

[b] Reference state at temperature T_{avg} is $\frac{1}{2}$ S_2(g).

TABLE 3

Heat of Sulfur Adsorption and Heat of Bulk Sulfide Formation for Ni, Co, Fe, Ru, and Pt

Metal	ΔH_f°[S(a)][a] ($kJ \cdot mol^{-1}$)	Avg. T (K)	ΔH_{f298}°[MeS(s)][b] ($kJ \cdot mol^{-1}$)
Ni	−249	863	−172.3
Fe	−197	826	−164.7
Co	−216	844	−170.7
Ru	−216	886	−167.3
Pt	−177	733	−147.4

[a] ± 20 $kJ \cdot mol^{-1}$ for half saturation coverage.

[b] From Ref. (15).

DISCUSSION

From measurements of the heats of adsorption, it is determined that the binding energy of sulfur adatoms on the surfaces of platinum crystallites decreases almost linearly with increasing coverage. With surface sulfur coverage normalized to CO adsorption at 300 K, the adatom binding energy[2] of chemisorbed sulfur (E_s) varies as $E_s = 448-205\ \xi_s$ ($kJ \cdot mol^{-1}$) for coverages from 0.1 to 0.6. The magnitude of the decrease in E_s with increasing coverage is considerably greater than that for Ni (*3*), Ru (*4*), and Co (*5*). A similar trend has been reported for sulfur adsorption on a single-crystal Pt(100) (*10, 11*).

Fischer and Kelemen (*11*) have analyzed the data of Heegemann *et al.* (*10*) for the time-dependent evaporation of chemisorbed sulfur from Pt(100). By assuming that the rate of sulfur loss was due to simple evaporation of sulfur atoms following the simple rate law, rate = $10^{13}\ s^{-1} \exp(-E_s/RT)$, they were able to estimate the binding energy of sulfur adatoms and determine the change in binding energy with sulfur coverage. The results of their analysis show even greater coverage-dependence of the binding energy of chemisorbed sulfur for Pt(100) than the present results for Pt crystallites. Assuming 1.1×10^{15} molecules CO adsorbed per cm^2 of Pt surface area, we can adjust the sulfur coverage (*11*) on Pt(100) to the scale used in this work.[3] We calculate from their data $E_s = 510-317\ \xi_s$ ($kJ \cdot mol^{-1}$), a result in good agreement with the present work.

A similar analysis can be performed for sulfur adatom desorption (*10*) from Pt(111). The initial value of E_s for Pt(111) is roughly 65 $kJ \cdot mol^{-1}$ less than E_s for Pt(100). Considering the differences in experimental technique and the assumptions made in calculating the binding energies, we conclude that the agreement between results obtained for the single-crystal desorption measurements and the present equilibrium measurements is quite good.

A correlation has been suggested (*13*) between the heats of formation of two-dimensional surface compounds and three-dimensional sulfides. In accord with this correlation, we compare the heats of adsorption measured at one-half saturation sulfur coverage for Ni, Ru, Fe, Co, and Pt with the heats of formation of correspond-

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[2] The energy required to remove a sulfur adatom to vacuum.

[3] We estimate that, for our sample, $\xi_s = 0.57$ corresponds to saturation coverage with sulfur adatoms, which amounts to about one-half monolayer based on CO adsorption with saturation coverage of 0.8 monolayer.

ing bulk metal sulfides (Table 3) (*14, 15*). The correlation shows that the two-dimensional sulfur layers have heats of adsorption (based on $\frac{1}{2}$ $S_2(g)$ as the reference state) somewhat greater (approximately 45 kJ mol^{-1}) than the heats of formation of the bulk sulfides.

The standard entropy for sulfur chemisorbed on Pt (Table 2) is surprisingly large and is nearly constant (106 ± 7 J mol^{-1} K^{-1}, leaving 87 J mol^{-1} K^{-1} to be accounted for by the vibrational modes of sulfur adatoms and by changes in the surface phonon distribution of the platinum substrate. With reference to our previous studies (*3–5*), only sulfur chemisorbed on iron exhibited values comparable to those for platinum. From previous estimates of the vibrational entropy of sulfur adatoms on Ni (*5*), we estimate about 50 J mol^{-1} K^{-1} to be accounted for by the vibrational modes of sulfur adatoms and by changes in the surface phonon distribution of the platinum substrate. Therefore, an entropy contribution of about 30 J mol^{-1} K^{-1} entropy is unaccounted for. Possibly the adsorption of sulfur weakens the metallic bonds of the nearest neighbor platinum atoms, thereby causing a shift in the vibrational frequency of surface Pt atoms.

In relating our results to the problem of catalyst deactivation by chemisorbed sulfur, we have calculated the threshold levels in terms of H_2S/H_2 ratios for various metal surfaces (Table 4). At half saturation coverage with chemisorbed sulfur (ξ_s = 0.29) where poisoning may be expected to cause a 70% decrease in catalytic activity (*16*), the H_2S/H_2 threshold levels on Pt are quite high relative to the base metals (Table 4), e.g., nearly 1 ppm at 773 K vs <10 ppb for nickel. However, at 575 K, a typical catalyst operating temperature, the poisoning threshold is still as low as 3 ppb.

TABLE 4

Poisoning Thresholds for Pt, Ni, Co, Fe, and Ru

Metal	P_{H_2S}/P_{H_2} (ppm)[a]		
	573 K	773 K	1273 K
Pt	3000×10^{-6}	350×10^{-3}	70
Ni	1×10^{-6}	4×10^{-3}	30
Fe	500×10^{-6}	90×10^{-3}	40
Co	2×10^{-6}	5×10^{-3}	30
Ru	10×10^{-6}	10×10^{-3}	20

[a] Reactive H_2S concentration for half saturation sulfur coverage at given temperature.

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