

Thermodynamics of Sulfur Chemisorption on Metals

V. Alumina-Supported Iridium¹

JON G. McCARTY AND H. WISE

Solid State Catalysis Laboratory, SRI International, Menlo Park, California 94025

Received August 29, 1984; revised March 15, 1985

The isosteric heats of adsorption of sulfur chemisorbed on iridium (dispersed on alumina) have been evaluated from measurements of the equilibrium $\text{Ir(s)} + \text{H}_2\text{S} \rightleftharpoons \text{Ir[S(a)]} + \text{H}_2\text{(g)}$ over a temperature range from 450 to 900 K. With increasing surface coverage the enthalpy of formation of the adlayer declines from a value of $\Delta H_f^\circ = -219$ to $-149 \text{ kJ} \cdot \text{mol}^{-1}$ [with $\frac{1}{2} \text{S}_2\text{(g)}$ as the reference state]. The heats of adsorption at low surface coverages of sulfur are correlated with the optical density of states at the Fermi energy for a number of metals studied. © 1985 Academic Press, Inc.

INTRODUCTION

Current studies on the adsorption thermodynamics of sulfur on different metal surfaces (1-4), have been extended to experimental measurements of the binding energy of sulfur adatoms on iridium crystallites dispersed on an alumina support. This data is of special importance, not only to the problem of sulfur poisoning of metal catalysts, but also to the elucidation of the relationship between the electronic interaction of the adatom with the substrate and the bond structure and coordination chemistry of the metal surface.

EXPERIMENTAL

The sulfur adsorption isosteres were determined from measurements of the concentration of H_2S (in 1 atm of H_2) in equilibrium with chemisorbed sulfur on Ir at different fractional surface coverages. The technique employed in this study has been described previously (1). Briefly, a small mass of sample containing iridium dis-

persed on alumina is placed in a quartz microreactor operating in a recirculation mode. The reactor is part of a closed-loop system which is constructed mainly of quartz with connecting tubing and valves made of fluorocarbon (Teflon). Sample valves are used to (1) inject a known mass of H_2S into the H_2 recirculating gas, and (2) withdraw gaseous aliquots for quantitative analysis of H_2S . For this analysis the gas aliquot is passed through a gas chromatographic column (made of Chromosil 310) to separate H_2S from the gas mixture. The H_2S eluting from the column is analyzed quantitatively with a photoionization detector (1) having a sensitivity of <1 ppb.

After establishment of the gas-surface adsorption equilibrium at a given temperature, the reactor temperature is changed and the $\text{H}_2\text{S}/\text{H}_2$ ratio in the recirculating gas monitored until the new equilibrium has been reached. The reversibility of the sorption process is determined by varying the temperature in both directions. Because the amount of adsorbed sulfur is greater by several orders of magnitude than the sulfur content in the recirculating gas stream, the transfer of sulfur from the surface to the gas phase is sufficiently small to have little effect on the surface coverage. Thus, the

¹ The support of this research by the Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy, is gratefully acknowledged.

TABLE 1

Sulfur Chemisorption Isosteres for Ir/Al₂O₃

θ Coverage	$-\Delta H_a$ (kJ · mol ⁻¹)	ΔS_a (J · mol ⁻¹ · K ⁻¹)	r^a	n^b
0.24	129.8 ± 10.2	-7.9	0.997	24
0.36	111.3 ± 5.9	+1.4	0.999	29
0.48	104.0 ± 16.7	-5.3	0.987	14
0.50	95.6 ± 13.8	+2.6	0.990	28
0.66	52.4 ± 5.0	+30.1	0.996	16

^a Correlation coefficient^b Number of equilibrium data points for each isostere.

isosteres for the adsorption equilibrium are readily determined.

The catalyst used contained 10 wt% iridium. It was prepared by impregnation of a calcined alumina support with an aqueous solution of IrCl₃. Preceding an adsorption experiment each catalyst sample (2 to 3 × 10⁻³ g) was loaded into the reactor and reduced stepwise in flowing hydrogen for 500 s at 400 K, 900 s at 580 K, 800 s at 720 K, and finally 90,000 s at 960 K. Subsequently, the system was isolated and the sample cooled to 773 K prior to introduction of an aliquot of H₂S/H₂ (1–3 vol% H₂S). The total adsorption capacity of the catalyst, determined from dynamic adsorption measurements of carbon monoxide on a freshly reduced catalyst sample at 300 K, amounted to 197 × 10⁻⁶ mol · g⁻¹ catalyst. In these measurements at atmospheric pressure, aliquots of CO/He (containing 1.2 × 10⁻⁸ mol CO per pulse) were injected into a He carrier stream and passed through the catalyst bed in a microreactor. The CO adsorbed in each pulse was evaluated by gas chromatography from the difference in CO concentration between the inlet and outlet to the reactor. Pulsing was continued until no further take-up of CO was detectable, i.e., saturation coverage had been attained.

RESULTS

Over the temperature range from 400 to 900 K we obtained the isosteres shown in Fig. 1. They span equilibrium partial pressure ratios of H₂S/H₂ from less than 1 ppb

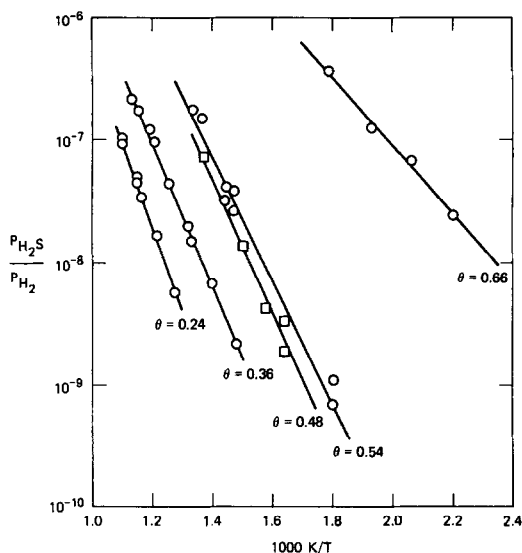


Fig. 1. Chemisorption isosteres of sulfur on Ir/Al₂O₃ (10 wt%).

to more than 10 ppm and surface coverages varying from 0.24 to 0.66 monolayers. Also typical Langmuir-type isotherms derived by interpolation and extrapolation of the data have been evaluated (Fig. 2). We have converted the CO-normalized surface coverage to absolute values by using a conversion factor of 0.5. This value is based on a comparison of a series of adsorption studies on Ir/Al₂O₃ with oxygen, hydrogen, and carbon monoxide (5).

By analysis of the isosteres as a function of temperature and surface coverage we can calculate the heats (ΔH_a) and entropies

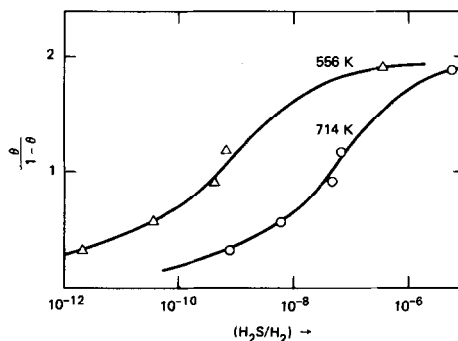


Fig. 2. Adsorption isotherms of sulfur on Ir/Al₂O₃.

TABLE 2

Enthalpy and Entropy of Formation ^a of Sulfur Chemisorbed on Ir/Al ₂ O ₃			
θ Coverage	$-\Delta H_f^\circ$ (kJ · mol ⁻¹)	S_f° (J · mol ⁻¹ · K ⁻¹)	T_{avg} (K)
0.24	219 ± 10	76	849
0.36	200 ± 6	84	779
0.48	192 ± 17	76	666
0.50	184 ± 14	84	679
0.66	149 ± 5	108	495

^a Reference state is $\frac{1}{2}$ S₂(g) at T_{avg} .

(ΔS_a) of adsorption of sulfur on Ir (Table 1) using the Van't Hoff equation. The results indicate a decline in the value of ΔH_a from -130 to -52 kJ · mol⁻¹. A decline in the exothermic heat of adsorption with sulfur coverage had also been observed for the other metals studied (1-4).

The isosteric heats of adsorption have been converted to the standard enthalpies ΔH_f° and entropies (S_f°) of formation for adsorbed sulfur, with $\frac{1}{2}$ S₂(g) as the reference state, by use of the relationship

$$\Delta H_f^\circ(T)[S(a)] = \Delta H_a(T) + \Delta H_f^\circ(T)[H_2S(g)],$$

where $\Delta H_f^\circ(T)[H_2S(g)]$ represents the standard heat of formation of gaseous H₂S. In these calculations the average temperature (T_{avg}) over the range of measurements was selected for each isostere. The results are summarized in Table 2.

TABLE 3

Sulfur Poisoning Thresholds^a for Alumina-Supported Ir, Pt, and Ni

Metal	H ₂ S/H ₂ in ppm			T (K) for 1 ppm H ₂ S/H ₂
	573 K	773 K	1073 K	
Ir	0.0026	0.47	30	814
Pt	0.039	1.5	27	746
Ni	9.0×10^{-5}	0.091	23	879

^a For 70% saturation sulfur coverage.

DISCUSSION

Graphic representation of the experimental results demonstrates that the adsorption thermodynamics of sulfur adatoms on Ir are similar in appearance to that of the other metals studied (Table 3) (1-4). The heat of formation of the adspecies (Fig. 3) per mole sulfur atoms declines from a value of -219 kJ · mol⁻¹ at low coverage to a value comparable to one-third of the heat of formation of bulk Ir₂S₃ (-131 kJ · mol⁻¹) at high coverage (6, 7). It is apparent that at low coverage, chemisorbed sulfur is thermodynamically more stable by at least 88 kJ per mole sulfur than the bulk sulfide. Similar characteristics are exhibited by other transition metal-sulfur systems (8, 9). The relatively small variation in the entropy values for the chemisorbed state (Table 2) counterindicates nonuniformity of the binding sites as a cause for the decline in the exothermic heat of adsorption with increasing coverage. Repulsive sulfur adatom in-

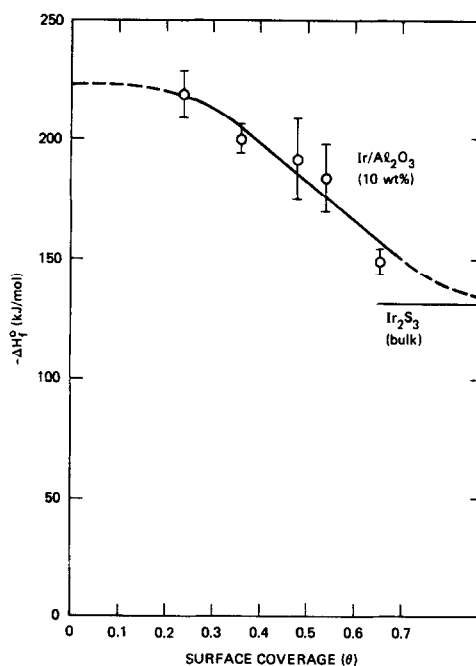


FIG. 3. Heat of formation of adsorbed sulfur on Ir/Al₂O₃ and Pt/Al₂O₃ as a function of fractional surface coverage. The heat of formation indicated for Ir₂S₃ is per mole of sulfur atoms.

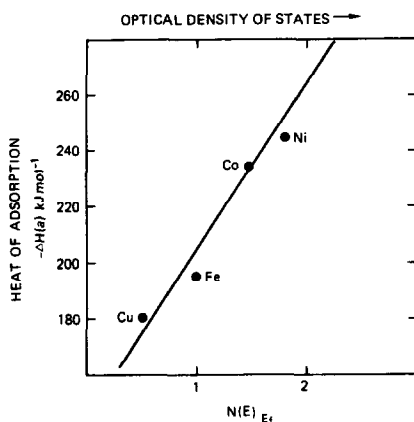


FIG. 4. Variation in heat of adsorption of sulfur with the optical density of states at the Fermi energy for several metals.

teractions with increasing coverage probably are the cause of the decline in sulfur adatom binding energy.

Recent measurements of angle-resolved photoemission spectra (ARPES) have demonstrated changes in the electron distributions curves induced by sulfur chemisorption for single-crystal surfaces of Cu (10) and Ni (11). In the case of Cu(100) the presence of chemisorbed sulfur causes a strong reduction in *d*-band and *sp*-band emission and the appearance of spectral features associated with sulfur 3*p* orbitals. For the low index plans of Ni [(100), (110), and (111)] the ARPES data demonstrate much stronger suppression of the *d*-band emission than for Cu. Also, the spectral feature associated with the atomic (3*p*) orbital of sulfur is prominent. The pronounced decline, broadening, and shift in the *d*-band peak to higher binding energies are indicative of the changes in substrate electronic structure induced by sulfur chemisorption.

In order to identify the surface orbitals of the metal substrate which are primarily re-

sponsible for bonding of sulfur, we have attempted a correlation between the heats of adsorption of sulfur at low coverage on various metals and their density of states (D-o-S) in the absence of an adsorbate as derived from photoemission spectra. In Fig. 4 we have plotted the heats of adsorption of sulfur at low surface coverage ($\theta < 0.2$) as a function of the optical D-o-S at the Fermi level for Fe, Co, Ni, and Cu, for which such data are available (12). A satisfactory linear correlation is obtained, indicative of the strong contribution of *d*-band orbitals to bond formation with sulfur adatoms. It is likely that this correlation extends to the second- and third-row metals through the participation of the *d*-band electrons of these metals in the binding of sulfur atoms.

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