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Kinetic Studies with a Sulfur-Tolerant Water Gas Shift Catalyst[1]

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Experimental measurements have demonstrated high water gas shift (WGS) activity for molybdenum sulfide-based catalyst in the presence of hydrogen sulfide. The defect structure of the catalyst, controlled by the sulfur activity in the gas phase, has a dominant effect on the reaction rate. The reaction kinetics are interpreted in terms of Langmuir–Hinshelwood surface reaction. The mechanism is shown to involve a redox cycle with Mo(V) as an important species in WGS catalysis. XPS measurements provide information on the reductive sulfidation of the catalysts from the Mo(VI)-oxide state.

I. INTRODUCTION

In SNG[3] production from coal-derived syn gas ($H_2/CO \leq 1$), the water gas shift (WGS) reaction plays an important role because it provides the additional hydrogen required for subsequent catalytic methanation (ME). The catalysts currently in use for WGS, such as Fe_3O_4/Cr_2O_3 (*1*), Cu (*2*), and Ru (*3*), readily catalyze the reaction between carbon monoxide and steam. However, their utility as well as that of the transition metal methanation catalysts (*4*) is severely limited by their sensitivity to sulfur poisoning. As a result the production of "sulfur-free" synthesis gas becomes an integral part of any process designed for sequential WGS and ME. Recently the development of more sulfur resistant ME catalysts has relaxed the stringent requirements for sulfur cleanup in the feed stream to the catalytic reactor (*5*). At the same time it has made desirable the development of WGS catalysts of significantly greater sulfur tolerance. In this study we wish to report on the catalytic properties of molybdenum sulfide for the WGS reaction. In earlier publications from this laboratory we demonstrated the close relationship between the electronic defect structure of this material and such catalytic reactions as hydrodesulfurization (*6*) and hydrogenation (*7*). We have extended the earlier studies to the WGS reaction with supported molybdenum sulfide catalysts.

II. EXPERIMENTAL DETAILS

A. *Catalyst Preparation*

The catalyst employed in this study was prepared by impregnation to incipient wetness of a high-surface-area alumina support (γ-alumina, 350 m^2/g) with an aqueous solution of ammonium heptamolybdate. Its concentration was adjusted to yield the desired weight loading of molybdenum (10 wt%). The catalyst sample was dried in a vacuum oven at 340 K, and calcined in flowing oxygen at 1 atm and 773 K. Pretreatment of the catalyst involved exposure for 17 hr at 773 K to a gas mixture of H_2S, H_2, and He. The H_2S/H_2 was varied over a range of compositions in order to examine the effect of sulfur activity on catalyst reactivity.

B. *Catalytic Measurements*

For the studies of catalytic WGS activity we employed a continuous-flow reactor containing the catalyst (0.025 to 0.050 g) on

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[3] The acronym SNG derives from "substitute natural gas."

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a glass frit inside a small Pyrex glass cylinder. The reactor was heated to the desired temperature by means of an external electrical furnace. The steam generator consisted of a pump that advanced the piston of a syringe and displaced liquid water through a fine needle onto a glass-enclosed heater wrapped with fiberglass. The water vapor so produced was carried away by the CO/He gas (10 vol% CO) flowing over the water vaporizer. The rate of water feed was adjustable to provide the desired concentration of steam in the gas mixture. Both the inlet and product stream could be diverted to a sampling loop and subjected to chemical analysis by gas chromatography (GC) for CO and CO_2. The GC column for separation of CO from CO_2 contained "Spherocarb" (80–100 mesh) and operated at 315 K. In addition, gas aliquots were analyzed quantitatively for sulfur-containing species (H_2S, COS, CS_2) by passage through a "Chromosil/310" column at 315 K and detection by means of a flame photometric analyzer.[4] The entire sampling system was wrapped with heating tape and heated to about 325 K to prevent condensation of water vapor.

III. RESULTS

A. *Sulfur Incorporation into the Catalyst*

As metal oxide the catalyst exhibited no measurable WGS activity. However, significant conversion of reactants became apparent after the catalyst had been exposed to H_2S/H_2. A series of measurements was carried out to elucidate the process of sulfur incorporation in the catalyst and its effect on WGS activity. In these studies the catalyst samples were exposed at constant temperature to flowing gas mixtures of H_2S and H_2 containing various concentrations of H_2S (500 to 5000 ppm b · vol). The amount of sulfur taken up by the catalyst was determined by measuring at regular time intervals the difference in H_2S concentration of the gas entering and leaving the reactor. By integrating the sulfur uptake with respect to exposure, we were able to calculate the total amount of sulfur retained by the catalyst during a given exposure.

During exposure of the catalyst to H_2S/H_2 gas mixtures a rapid uptake of sulfur was noted until the Mo/S ratio approached approximately unity, assuming a uniform distribution of sulfur throughout the catalyst sample. This stage was followed by a less rapid rate of sulfur incorporation with the S/M ratio attaining values ranging from 2.0 to 2.4, at which time no more sulfur uptake was detectable. This pattern of sulfur addition to the catalyst prevailed irrespective of the H_2S level in the gas stream within the range of our experimental measurements (<5000 ppm H_2S in H_2).

B. *WGS Activity*

In the evaluation of the catalytic properties for WGS the following experimental parameters were investigated: (a) conversion at different H_2S levels in the feed gas, (b) catalytic activity as a function of H_2O/CO ratio in the inlet stream, and (c) conversion at different temperatures.

For our studies of the role of sulfur activity on the rate of WGS, the H_2S level was kept at the same value during presulfidation and catalytic reaction. The experimental results (Fig. 1) demonstrate a strong influence of sulfur activity on the steady-state WGS reactivity. A continuous rise in WGS conversion was observed with increasing sulfur activity.

As for CO_2 formation as a function of H_2O/CO inlet ratio at a constant H_2S level, the reaction rate was found to go through a maximum (Fig. 2). In these experiments the CO concentration in the feed stream was kept constant but that of H_2O was varied. Similar behavior was exhibited by both catalysts.

To identify the catalytic component active in WGS, we compared with activity of presulfided Al_2O_3 and MoO_3/Al_2O_3. The results shown in Table 1, demonstrate une-

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[4] Manufactured by Tracor, Inc.

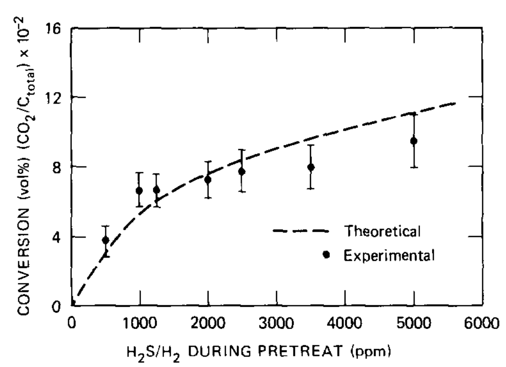


FIG. 1. Water gas shift conversion for different sulfur activities of catalyst pretreated in H_2S/H_2. Space velocity = 1.4×10^6 hr^{-1}; temperature = 723 K; CO feed rate = 10×10^{-4} mol/min; H_2O feed rate = 2.5×10^{-4} mol/min.

quivocally that the molybdenum sulfide component is responsible for the observed WGS activity.

IV. DISCUSSION

It is quite apparent that the molybdenum sulfide-based catalysts provide excellent WGS activity in the presence of hydrogen sulfide. The typical WGS conversion rate of 3×10^{17} molec · cm^{-2} · s^{-1} (based on the data of Fig. 2 with 0.05 g catalyst and a BET surface area of 60 m^2 · g^{-1} catalyst) compares most favorably with the rates obtained with chromia–alumina and iron oxide–chromia catalysts (*8*).

As for the mechanism of the WGS reaction the kinetic data are interpretable in terms of a surface reaction of the Langmuir–Hinshelwood type. The reaction rate r_1 is governed by the adsorption probability of each reactant, which in turn, is proportional to the surface coverage of each reactant (θ):

$$r_1 = k\theta_{H_2O}\theta_{CO}, \quad (1)$$

where k is the rate constant for WGS. Using the Langmuir adsorption isotherm, we can write for the fractional surface coverage for each adspecies:

$$\theta_{H_2O} = K_1[H_2O]/\{1 + K_1[H_2O] + K_2[CO]\}, \quad (2)$$

$$\theta_{CO} = K_2[CO]/\{1 + K_1[H_2O] + K_2[CO]\}. \quad (3)$$

K_1 represents the equilibrium constant for H_2O adsorption, and K_2 that for CO adsorption; the square brackets indicate the gas-phase concentrations of each of the reactants. By substitution into Eq. (1) one obtains for the WGS reaction rate:

$$r_1 = kK_1K_2[CO][H_2O]/\{1 + K_1[H_2O] + K_2[CO]\}^2. \quad (4)$$

Thus, if the [CO] is kept constant and the $[H_2O]$ is varied, the value of r_1 increases linearly at first, then passes through a maximum at the point where $K_1[H_2O] = 1 + K_2[CO]$ or $K_1[H_2O] \simeq K_2[CO]$ for $K_2[CO] \gg 1$. Indeed, our kinetic measurements of WGS exhibit a maximum (Fig. 2), indicative of the displacement of CO adspecies by the more strongly bound H_2O adspecies as the $[H_2O]$ is increased. At low concentra-

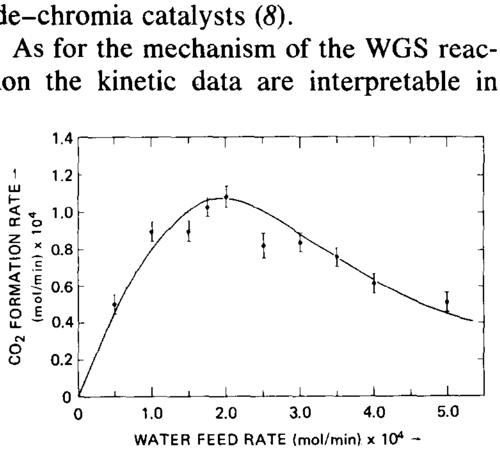


FIG. 2. Rate of water gas shift reaction as a function of water concentration at 733 K. (CO feed rate = 8.0×10^{-4} mol/min; space velocity = 1.4×10^6 hr^{-1}; 2500 ppm H_2S.)

TABLE 1

Water Gas Shift Activity[a] of Different Catalysts Components at 723 K

Catalyst component (cation)	Fractional conversion (vol%)
Al	0
Mo/Al	58

[a] Experimental conditions: $H_2O/CO = 1.1$; pressure = 1 atm; VHSV = 27,000 hr^{-1}; H_2S = 2500 ppm.

tion of H_2O relative to CO, the rate reduces to

$$r_1 = kK_1K_2[H_2O][CO]/\{1 + K_2[CO]\}^2 \quad (5)$$

for $K_2[CO]^2 \gg 1$ and one obtains

$$r_1 \simeq kK_1[H_2O]/K_2[CO]$$

indicating that under these conditions the WGS rate is proportional to the water concentration and inversely proportional to the carbon monoxide concentration, as evidenced in our experimental measurements. Conversely, at high $[H_2O]$ so that $\{1 + K_1[H_2O] + K_2[CO] \simeq K_1[H_2O]\}$:

$$r_1 \simeq kK_2[CO]/K_1[H_2O]. \quad (6)$$

From a series of rate measurements of the type shown in Fig. 2, we were able to obtain the variation with temperature of the rate constants for the WGS reaction (Table 2), from which was derived an activation energy of 53.6 kJ/mol (12.8 kcal/mol) for the WGS reaction, a value comparable to that observed for an iron oxide catalyst (*2*). Also from the ratio of the equilibrium constants K_1/K_2 (Table 2), we can calculate the difference in free energy of adsorption of water and CO on the catalyst during WGS.

We employed X-ray photoelectron spectroscopy (XPS) to determine the oxidation state of Mo in the fresh and sulfided catalysts and the degree of interaction between the various components in the sample. The binding-energy values (BE) derived from the XPS results (Table 3) were referenced to the C(1*s*) peak (BE = 284.6 eV). We selected for detailed analysis the following lines: Mo($3d_{5/2}$); Al(2*p*); O(1*s*); C(1*s*); S(2*p*). In the interpretation of the oxidation of Mo we used the results reported by Patterson *et al.* (*12*).

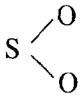
TABLE 2

Values of Kinetic and Thermodynamic Parameters for WGS Reaction[a]

Temperature (K)	Rate constant k (mol/min) × 10^4	$\frac{K_1}{K_2}$	Difference in free energy of adsorption $\Delta G^0_{H_2O} - \Delta G^0_{CO}$ (kcal/mol)
648	0.45	3.2	−1.5
723	1.20	5.0	−2.3
773	1.86	4.0	−2.1

[a] Space velocity = 2.2×10^5 hr^{-1}.

The fresh catalysts, containing the oxides of Mo and Al, indicated the prevalence of Mo(IV) (BE = 232.9 eV), Mo(V) (BE = 231.5 eV), and Al(III) (Table 3). After exposure to H_2S/H_2 the XPS results indicate the presence of MoS_2 [BE Mo(IV) = 229.0 eV, BE $(S)^{2-}$ = 161.9 eV], and Mo(V) (BE = 231.3 eV). Apparently the pretreatment and/or exposure to feed has resulted in the disappearance of Mo(VI) and the formation of Mo(V)[5] in admixture to Mo(IV). The presence of a sulfur–oxygen bond (BE = 531.4 eV) in the sulfided sample may be due to an



surface species formed by exposure to air.

Heating of the catalyst $MoO_3/\gamma\text{-}Al_2O_3$ under vacuum above 700 K leads to the formation of Mo(V). Reduction in H_2 at these temperatures yields Mo(IV), but not Mo(III) or lower valence states. Thus the Al_2O_3 support appears to stabilize the Mo(V) valence state and limit reduction (*10*). Also conversion of MoO_3 to MoS_2 by way of a Mo(V) intermediate is kinetically more rapid than prereduction of MoO_3 to MoO_2 and subsequent sulfidation to MoS_2 (*11*).

A relationship may be sought between the XPS-derived evidence for the presence of Mo(V) and the interpretation of the electronic properties of the catalyst in terms of its defect structure.

As shown by the data in Fig. 1 the catalytic properties for WGS significantly improved with increases in sulfur activity of

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[5] The formation of Mo(V) has been identified by electron spin resonance during sulfidation of the catalysts under study (9).

TABLE 3

Selected Binding (eV) Energies Measured by XPS[a]

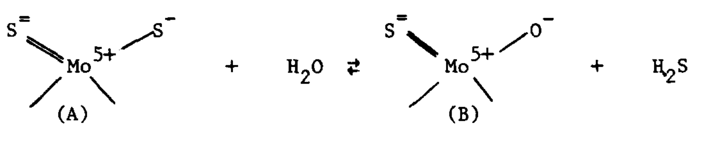
Sample	Mo($3d_{5/2}$)	Al($2p$)	O($1s$)	C($1s$)	S($2p$)
Fresh catalyst	232.9 (VI) 231.5 (V)	73.9	529.7	284.6 288.4[b]	—
Sulfided catalyst[c]	231.1 (V) 229.0 (IV)	73.8	529.6 531.4[d]	284.6 288.4[b]	161.9
MoO_3[e]	232.5 (VI)	—	531.1	284.3	—
MoO_2[e]	229.4 (IV)	—	—	530.8	—
MoS_2[e]	228.9 (IV)	—	—	284.8	162.2

[a] Referenced to C(1*s*) peak (BE = 284.6 eV).
[b] C–O bond.
[c] After 16-hr exposure to 2500 ppm H_2S in H_2 at 823 K.
[d] S–O bond.
[e] T. A. Patterson *et al.*, *J. Phys. Chem.* **80**, 1700 (1976).

the solid, as brought about by pretreatment in gas mixtures containing progressively higher concentrations of H_2S in H_2. The results exhibit a square-root dependence on H_2S/H_2 as shown by the broken curve in Fig. 1. One may interpret these data in terms of the solid-state defect structure (*6, 7*) of the molybdenum sulfide system which is capable of forming a wide range of solid solutions ($Mo_{1-x}S_2$) in which the ratio of Mo/S deviates from the stoichiometric value of MoS_2 ($x = 0$). As a result, the solid-state properties of the material can range from n-type semiconductivity ($x < 0$) to p-type conductivity ($x > 0$) depending on the sulfur activity in the gaseous environment with which the catalyst is in dynamic equilibrium. For the layer-type crystal structure exhibited by molybdenum sulfide, rapid transport of sulfur ions would be expected, so that at the temperatures of interest to WGS the defect structure of the solid phase would rapidly approach conditions of steady state.

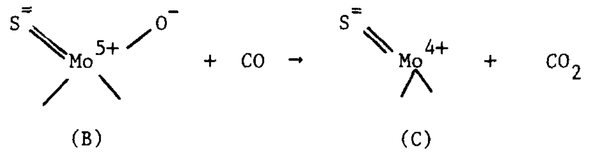
The WGS reaction mechanism in the presence of molybdenum sulfide needs to take into account the following observations made during the course of our study: (1) as a hexavalent oxide molybdenum exhibits little or no WGS activity, (2) during sulfidation by exposure to H_2S/H_2 mixtures under our experimental conditions Mo oxide is converted to a sulfide containing Mo(IV) and Mo(V) depending on the thermodynamic sulfur activity at the gas/surface interface, (3) the catalytic WGS activity of the sulfided catalyst is related to its defect structure in terms of its electronic hole density, or its equivalent in terms of Mo(V) cation density, (4) with increasing H_2O/CO ratio the catalytic rate passes through a maximum beyond which water inhibits the WGS reaction.

Of special interest is the apparent correlation between the Mo(V) cation density and catalytic activity. We are led to suggest that this valence state and coordination of Mo(V) permit a rapid exchange of the sulfur ligand (S^-) by oxygen (O^-) in the coordination sphere of the Mo ion:



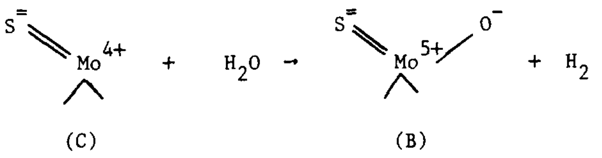
(7)

Indeed the reversible formation of H_2S on exposure to water of the sulfided Mo catalysts has been observed under conditions favoring the presence of Mo(V). For WGS, subsequent reaction of species (**B**) with CO leads to CO_2 formation and reduction of Mo(V) to Mo(IV):



(8)

Species (**B**) is recycled by exposure of (**C**) to water vapor:



(9)

In the case of molybdenum oxide, Mo(IV) is readily oxidized by water and the formation of Mo(V) has been observed by electron spin resonance spectroscopy (*13*). We conclude that the unique property of molybdenum sulfide in catalyzing the WGS reaction in the presence of sulfur-containing feed gas is based on a redox cycle involving Mo(IV)/Mo(IV).

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