ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

Technical Progress Report for the Period

December 1991-February 1992

Kamil Klier
and
Richard G. Herman
with
Michelle Richards-Babb

Zettlemoyer Center for Surface Studies
and Department of Chemistry
Lehigh University
Bethlehem, PA 18015

March 1992

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY-Pittsburgh Energy Technology Center

Under Contract No. DE-FG22-91PC91301

U.S.-DOE Patent Clearance is not required prior to
the publication of this document.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

Disclaimer

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

OBJECTIVE AND SCOPE OF WORK

The objective of the proposed research is to investigate and develop a novel catalytic process for the conversion of coal-derived synthesis gas into high octane C_1 - C_4 alcohols, especially ethanol, by a highly selective and efficient pathway.

The catalysts chosen fall into the general category of bifunctional, base-hydrogenation, sulfur-tolerant chalcogenides with a heavy alkali (K^+ , Rb^+ , Cs^+) component dispersed on their surfaces. The alkali base activates CO and CO_2 by an associative mechanism that does not rupture the C-O bond and the transition metal chalcogenide, primarily sulfide, activates hydrogen for the reduction of HCO_x intermediates (viz. formate $HCOO^-$) to alcohols. The combination of the two functions also greatly promotes the water gas shift (WGS) reaction, and a novel class of low temperature, sulfur-tolerant WGS catalysts ensues. Different sulfides possess different hydrogen activation ability, viz. $RuS_2 > MoS_2 > NbS_2$. The product alcohols are potential precursors of undesired hydrocarbons (e.g. methanol or methane) and actually not the highest but rather optimum hydrogenation ability of the catalyst is desired. An important guide to finding such an optimum is reaction kinetics, particularly with respect to hydrogen, which is proposed to be investigated here along with establishing selectivity patterns in the presence of CO_2 , H_2O , and H_2S (Tasks 1 and 2). The water gas shift (WGS) process, which is operated under less severe conditions than the alcohol synthesis, also requires a balance between the basic and hydrogenation/dehydrogenation function, including hydride abstraction from the formate $HCOO^-$, and the optimum balance between the two functions for WGS and alcohol synthesis is generally different. It is proposed to establish the optimum process conditions and catalyst compositions for WGS and alcohol

synthesis in terms of reaction pressure, temperature, and alkali/TS₂ ratio for T = Nb, Mo, and Ru (Task 3).

The above tasks are greatly assisted by solid state and spectroscopic investigations of the catalyst and the surface intermediates (Task 4), including the highest available resolution valence band XPS spectroscopy, which is carried out in the SCIENTA ESCA-300 laboratory at Lehigh University. Other instrumental techniques that will be utilized include X-ray powder diffraction, Auger spectroscopy, SEM, HR-TEM, FTIR, NMR, and optical DRS, including exciton spectroscopy.

The impact of the current research promises to be (i) to develop a novel process for ethanol, (ii) to develop a novel low temperature sulfur-resistant WGS catalyst and process, (iii) to establish kinetic laws for the above processes, and (iv) to determine patterns and modes of activation of the reaction components, as well as gaseous promoters, such as CO₂, H₂O, and H₂S, on the rates and selectivities of the WGS and alcohol synthesis processes. The alcohol fuel so produced can also be converted, partially or totally, to high octane ethers, e.g. ethanol to ETBE. Therefore, the proposed research is directed to the synthesis of an alternative clean high octane liquid fuel in which all carbon originates from coal.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

SUMMARY OF TECHNICAL PROGRESS

Last quarter new RuS_2 and NbS_2 catalysts were prepared, characterized, and tested for hydrocarbon and alcohol synthesis activity in the temperature range of 275–325°C and at ≈ 82 atm pressure with $\text{H}_2/\text{CO} = 1$ synthesis gas. Under these reaction conditions, the RuS_2 catalysts were observed to be much less active than were the MoS_2 -based catalysts. It was also found that in the preparation of the niobium sulfide catalysts by a variety of methods, sub-stoichiometric materials, in terms of the bulk stoichiometry, were synthesized. However, a surface stoichiometry of $\text{NbS}_{2.01}$ was determined by X-ray photoelectron spectroscopy analysis. Catalytic testing of these materials after doping with cesium resulted principally in the formation of hydrocarbons, mainly CH_4 , and CO_2 from $\text{H}_2/\text{CO} = 1$ synthesis gas. These catalysts did not exhibit appreciable activity and the yields were < 2 g/kg catal/hr, e.g. the $\text{Cs}/\text{NbS}_{1.4}$ catalyst was ≈ 20 less active per unit surface area as the Cs/MoS_2 catalyst.

To gain insight into the surface chemistry of this class of catalysts, to probe their stabilities in reducing and oxidizing environments, and to obtain guidance in the design of active and stable transition metal sulfide catalysts under necessary reaction conditions, high resolution surface analyses by X-ray photoelectron spectroscopy and theoretical computations have been carried out. The results of these studies are summarized in this quarterly report.

ETHANOL SYNTHESIS AND WATER GAS SHIFT OVER BIFUNCTIONAL SULFIDE CATALYSTS

TECHNICAL PROGRESS

Discussion of Thermodynamic Stability

The stability of a catalyst under the reactor conditions employed is very important in any investigation into the development of a new catalyst system. Previous catalytic studies on alkali doped MoS_2 have shown that this catalyst is stable for long periods of time at pressures of 81.6 atm and temperatures ranging from 250°C to 350°C .¹ However, knowledge about the stability of related transition metal disulfide systems is unavailable experimentally. For this reason an investigation of the thermodynamic properties of the third, fourth, and fifth period transition metal disulfides, TS_2 , has been carried out. In the reactor, H_2 gas is present as one of the reactants in the synthesis gas used for higher alcohol synthesis over these catalysts. The water gas shift (WGS) reaction and production of hydrocarbons are both reactions that can produce H_2O (or consume H_2O in the case of the WGS reaction) in the reactor. For these reasons, the stability of the catalyst in a hydrogen environment towards its corresponding metal and most stable sulfide and oxide forms is valuable information. This information can be calculated from available thermodynamic data.²⁻⁴

The overall reaction for the reduction of transition metal disulfides by H_2 is shown in Equation 1. Calculated Gibbs free energies at 298K and 1 atm

pressure are shown in Figure 1. The most stable TS_2 compounds will be the ones with the most positive ΔG values. As can be seen from the trends in Figure 1, the stability of the TS_2 toward its corresponding metal, T, decreases as one proceeds across each period. The most stable compound having a layered structure is NbS_2 , while the most stable pyritic compound is RuS_2 . In general the most

FIGURE 1

Stability of TS_2 Toward Reduction ($T=298K$, 1atm)

stable compounds are found in the fourth period.

When the stability of the TS_2 compounds are compared to the corresponding most stable oxide forms, the trend is markedly different. The general overall reaction for oxidation of the TS_2 compounds is shown in Equation 2. Calculated

Gibbs free energies at 298K and 1 atm pressure are shown in Figure 2. Again, the most stable TS_2 compounds will be the ones with the most positive ΔG values. As can be seen from Figure 2, the layered compounds NbS_2 and TaS_2 are very unstable toward oxidation to Nb_2O_5 and Ta_2O_5 , respectively. Also, the third period TS_2 compounds are only moderately stable toward oxidation to Mn_3O_4 and $Fe_3O_4(Fe_2O_3)$. As can be seen from the trends in Figure 2, the stability of the TS_2 compounds toward oxidation increases as one proceeds across each period. This trend is opposite to that found for reduction. Again, the fourth period TS_2 compounds are the most stable. Since the trends in stability are opposite for the two tests of reducibility and oxidizability, both stability criteria must be considered when choosing a catalyst. From this analysis, compounds with intermediate values of Gibbs free energy for both reduction and oxidation should be the most stable under the catalytic conditions employed. For example, the layered compounds MoS_2 , WS_2 , and ReS_2 and the pyritic compound RuS_2 should be the most stable compounds.

Precaution must be observed when analyzing the thermodynamic calculations presented in the preceding paragraphs. The calculations presented were obtained by using the thermodynamic values of bulk TS_2 compounds. However, the active portion of a catalyst is actually the surface and not the bulk. The surface may consist of atoms with dangling bonds and unshared vacancies, and thus surface thermodynamics may be different from those of the bulk. However, to a first approximation the trends exhibited for the bulk can be assumed to be similar for

FIGURE 2

Stability of TS_2 Toward Oxidation ($T=298K, 1atm$)
 $MS_2(s) + (y/x)H_2O \xrightarrow{\quad} (1/x)M_xO_y(s) + 2H_2S(g) + [y/(x-2)]H_2(g)$

the surface. An increase in pressure will not affect the reduction and oxidation reactions since the number of moles of reactant and product gases is equal.

Investigation of Electron Structure

Investigations into the electronic structure of TS_2 compounds is important for an understanding of the catalytic mechanisms occurring at the surface. An understanding of the electronic structure at the catalyst surface is important when considering the interaction of an adsorbate with the catalyst surface. For example, in the formation of C_1 - C_4 alcohols over Cs-doped MoS_2 , the electronic interaction of H_2 with the surface of MoS_2 is an important issue. The Cs-doped MoS_2 system has been extensively studied in terms of catalytic activity but little is known about the method in which hydrogen is activated on the surface. Electronic studies characterizing the surface properties of MoS_2 may shed some light on the nature of hydrogen activation.

A good experimental method of studying trends in the electronic structure of disulfide surfaces is by core level and valence band analysis via high resolution electron spectroscopy for chemical analysis (HR-ESCA), also called high resolution X-ray photoelectron spectroscopy, HR-XPS. HR-ESCA is a surface sensitive technique that can provide information on the oxidation state and chemical environment of surface species. Analysis of the valence bands via HR-ESCA can also lead to information on the highest occupied bands, which will most likely interact with specific adsorbates such as H_2 . In general since the TS_2 compounds are fairly covalent, the valence bands obtained via HR-ESCA are combinations of the atomic valence levels of sulfur and the transition metal. The experiment does not resolve the valence band into contributions due to the atomic valence levels from different atoms. Theoretically calculated valence bands can be used to interpret the HR-ESCA experimental results. A solid state adaptation of the extended Hückel theory is a very simple method that will

calculate the density of states, as well as the contributions of the valence atomic orbitals to the density of states. The package used for these types of calculations is entitled Extended Hückel Molecular, Crystal and Properties Package.⁵ This theory has been used to calculate the valence bands of representative transition metal disulfides, with some encouraging initial results. Thus, trends in the electronic structure of the disulfides can be studied in detail. Surface band structure can be theoretically investigated by setting up models with translational periodicity parallel to the surface, with the surface atoms in their regular or relaxed lattice positions, and the theory compared with experimentally determined band structures.

Input parameters necessary for calculating a specific TS_2 density of states are the following: x, y, z coordinates of the atoms in one unit cell; Slater type orbital exponents, ζ_1 , and coefficients, c_1 ; atomic ionization potentials, H_{11} ; and the k -points (wavevector) and weighting factor at which the calculation is to be carried out. Thus, the input parameters, specifically the atomic ionization potentials and Slater-type coefficients can be parametrized with respect to experiment. For instance, once the S 3s, 3p H_{11} , ζ_1 and c_1 parameters are found for one TS_2 compound, e.g. MoS_2 , these parameters can be used in a study of the electronic properties of a series of TS_2 compounds.

The program gives a density of states that cannot be compared directly to the valence band obtained via HR-ESCA. The ability of photoelectrons to be detected in the instrument depends on the incident X-ray energy and the atomic level and specific atom type from which the photoelectron originates. Thus, the experimental valence band could be considered to be a density of states modified by the photoelectron cross-sections of the atomic orbitals. Therefore, a theoretical valence band must be compared to the experimental valence band. A theoretical valence band can be obtained from the atomic orbital contributions to the density of states (AOPOP's). These atomic orbital contributions (AOPOP's)

are multiplied by their corresponding photoelectron cross-sections to obtain modified AOPOP's. The modified AOPOP's are then summed at each energy to obtain the theoretical valence band that can be compared directly to experiment. In the case of MoS_2 , the Mo 4d to S 3p photoelectron cross-section ratio is 4.08. Therefore, the Mo 4d AOPOP will be multiplied by a factor of 4.08 as compared to the S 3p AOPOP, resulting in a large contribution of the Mo 4d atomic orbitals to the valence band region.

The experimental HR-ESCA valence band regions of MoS_2 and NbS_2 are shown in Figure 3 and 4, respectively. The difference in the two disulfides can be seen immediately at the top of the valence band. The intensity of the peak at the top of the NbS_2 valence band relative to the rest of the valence band is less than in the case of MoS_2 . NbS_2 (Nb^{+4} , d^1 system) is a metal and has the highest occupied crystal orbital (HOCO) only half-occupied. MoS_2 (Mo^{+4} , d^2 system) is a small band gap semiconductor and has the HOCO fully occupied by electrons. Theoretical valence bands that have been parametrized and modified by the photoelectron cross-sections are shown in Figure 5 and 6 for MoS_2 and NbS_2 , respectively. The theoretical valence bands reproduce the experimental valence bands very well. The dispersion of the S 3s region is in good agreement between theory and experiment. The four-peaked nature and width of the upper portion of the valence band is reproduced theoretically. From experience manipulating the program, it has been found that the most important feature in obtaining an accurate description of the upper portion of the valence band is the radial extent of the S 3p atomic orbitals. If the S 3p Slater-type atomic orbitals are not highly diffuse, small overlap between the S 3p and Mo 4d atomic orbitals in the MoS_2 lattice will result in a 3-peaked valence band. However, more diffuse S 3p atomic orbitals produce the required overlap needed to give the valence band its 4-peaked nature. On comparison of the theoretical valence bands of MoS_2 and NbS_2 a question might arise as to the difference in the dispersion of the S 3s

FIGURE 3

Valence band region of polycrystalline MoS₂ shifted by 4.12 eV (work function, 4.1 eV; calibration, 0.02 eV).

Pass energy
75 eV

Slit width
1.1 mm

Energy step
0.05 eV

Det. height
60 %

Lens mode
TRANSMISSION

X-ray power
4.0 kW

Rec. time
03:23:16

Binding Energy [eV]

SCIENTA

FIGURE 4

Polycrystalline NbS(2-x). Valence Band Region.
VALENCE1 LEHIGH

Pass energy 75 eV
Slit width 1.1 mm
Energy step 0.05 eV
Det. height 90 %
Lens mode TRANSMISSION
X-ray power 7.4 kW
Rec. time 04:11:32

FIGURE 5

Valence band region of polycrystalline MoS₂ shifted by 4.12 eV (work function, 4.1 eV; calibration, 0.02 eV).

Pass energy	75 eV
Slit width	1.1 mm
Energy step	0.05 eV
Det. height	60 %
Lens mode	TRANSMISSION
X-ray power	4.0 kW
Rec. time	03:23:16

Binding Energy [eV]

SCIENTA

FIGURE 6

Polycrystalline NbS(2-x), Valence Band Region.
VALENCE1 LEHIGH

Pass energy 75 eV
Slit width 1.1 mm
Energy step 0.05 eV
Det. height 90 %
Lens mode TRANSMISSION
X-ray power 7.4 kW
Rec. time 04:11:32

Binding Energy [eV]

region. In MoS_2 , the theoretical dispersion is greater because of the smaller lattice constant, 3.16 Å, that separates the sulfur atoms within each S atomic layer. In NbS_2 , the theoretical dispersion is smaller because of the larger lattice constant, 3.31 Å, that separates the sulfur atoms within each S atomic layer.

A better understanding of the experimental valence band can be achieved by analysis of the theoretical modified AOPOP's. Shown in Figure 7 are the modified AOPOP's (Mo 4d, S 3s, and S 3p) for MoS_2 . Thus, the S 3s atomic orbitals are mainly the cause of the dispersion of the peak located at approximately 17.8 eV. The top of the valence band and (HOCO) located at approximately 6.0 eV is made up mainly of Mo 4d character. This character is usually referred to as d_{z^2} . However, an analysis of the atomic orbital coefficients that make up the crystal orbitals shows that the Mo 4d AOPOP consists of a considerable amount of $d_{x^2-y^2}$ and d_{xy} as well as d_{z^2} character. The covalent nature of MoS_2 can be seen in the large amount of mixing in the remainder of the valence band between the S 3p and Mo 4d atomic orbitals.

Now that the electronic structure of the bare MoS_2 surface has been investigated theoretically, predictions as to probable adsorption sites can be made. Studies under way at this time involve the adsorption of hydrogen on the MoS_2 surface both theoretically and experimentally. Theory, when compared to experiment, will lead to the identification of catalytic activation sites and insight into the mechanism of hydrogen adsorption.

FIGURE 7

Theoretical Valence Band
2-D MoS₂ (#171 kp)

REFERENCES

1. K. Klier, R. G. Herman, G. W. Simmons, C. E. Lyman, J. G. Santiesteban, M. Najbar, and R. Bastian, "Direct Synthesis of Alcohol Fuels Over Molybdenum-Based Catalysts," Final Technical Report DOE/PC/80014-F (December 1988).
2. I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, New York, (1973).
3. I. Barin, O. Knacke, and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances-Supplement," Springer-Verlag, New York (1977).
4. K. C. Mills, "Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides," Butterworths & Co., London (1974).
5. M.-H. Whangbo, M. Evain, T. Hughbanks, M. Kertesz, S. Wijeyesekera, C. Wilker, C. Zheng, and R. Hoffmann, "Extended Hückel Molecular, Crystal and Properties Package," QCPE 571.

END

DATE
FILMED

6126192