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Fundamental studies of hydrogen chemisorption on supported monometallic and bimetallic catalysts using microcalorimetry

by

Ramanathan L. Narayan

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Ames Laboratory, U.S. DOE
Iowa State University
Ames, Iowa 50011

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GENERAL INTRODUCTION

Supported catalysts

Highly dispersed transition metal catalysts are used in numerous commercial processes such as hydrocarbon conversions. For example, the use of Pt supported on acidic alumina or silica-alumina for reforming of naphtha in the production of gasoline is well known [1]. Another use of supported catalysts is in automobile emission control where supported Pt-Rh bimetallic catalysts are used. Supported Ru can be used in Fischer-Tropsch synthesis for the production of higher hydrocarbons from synthesis gas [1]. While many of these catalyst systems have been in commercial operation for several decades there is still a lack of consensus regarding the exact role of the catalyst on a molecular level. In particular, little is known about the mechanisms operating on the catalyst surface at the high pressure and high temperature conditions typically used in commercial operations. Furthermore, reliable information on the energetics and kinetics of processes at high pressures is lacking. A significant proportion of the high pressure thermodynamic data has been obtained by extrapolation of results obtained from "surface science" studies where single crystal metals are studied in high and ultra-high vacuum. While these surface science studies have provided valuable insight into the mechanisms operating on single crystals at low pressures [2], they do not account for phenomena, like mobility on the metal and spillover to the support, which may play a significant role on supported catalysts, particularly at high pressures [3].

An example of one such catalytic phenomena which continues to be an enigma to researchers in this field is the role of alkali promoters in Fischer-Tropsch synthesis. It has been found that adding alkali promoters to Fischer-Tropsch synthesis catalysts produces heavier hydrocarbons while reducing the rate of the reaction [1]. Though the role of alkali promoters has been investigated using numerous surface science techniques [5] there is still no agreement regarding the exact mechanism by which alkali produce these effects. The important theories proposed to explain the role of alkali promoters include electronic effects, site blocking, chemical interactions between alkali and adsorbates, alkali induced surface restructuring, and reduced mobility of reactants in the presence of alkali (for example, see [5] and references therein). To date most of the studies on Fischer Tropsch synthesis have focused upon the interaction between the alkali and CO. There have been few studies of the influence of alkali on the amounts and energetics of hydrogen chemisorption, especially at high pressures. Thus, in this work, discussed in Chapter 1, the energetics and extents of hydrogen chemisorption on Ru/SiO_2 and $K/Ru/SiO_2$ were investigated to elucidate the influence of the alkali promoter. A home-built microcalorimeter was used to investigate the thermodynamics of hydrogen chemisorption.

In order to understand the role of alkali promoters, the model Ru-Ag bimetallic catalysts were also investigated because Ag, relative to K, is inert. Further, Ag selectively blocks sites on the catalyst surface [6]. Thus, it was proposed that the theory of site blocking, proposed to explain the role of alkali promotes, could be investigated in detail.

Other elements are also added to the supported transition metal catalyst to improve the stability and/or selectivity of the catalyst. If the second element added is Ag or Cu then model catalysts are produced. Such model bimetallic systems are relatively simple to study [7] and contribute to the understanding of catalytic processes, particularly the role of surface structure on reactivity. To date there have been no fundamental investigations of the energetics and nature of hydrogen chemisorbed on these catalysts at high pressures. It was proposed that these characterization studies would elucidate the influence of catalyst structure on hydrogen chemisorption. At low concentrations Ag and Cu preferentially occupies edges, corners and other low metal coordination sites [6]. An important difference between Ag and Cu is that the former does not accommodate hydrogen which is a common probe used to characterize supported metal catalysts. In Chapter 2 the study of hydrogen chemisorption on silica supported Ru-Ag, Ru-Cu and Ru is presented.

Hydrogen chemisorption on transition metals has been extensively investigated by numerous workers [5,8,9,15,16 and references therein]. However, there have been few studies to investigate the hydrogen chemisorption behavior of supported Group VIII catalysts at high pressures. In Chapter 3 the energetics of hydrogen chemisorption on Ru/SiO_2, Rh/SiO_2 and Pt/SiO_2 was investigated to probe the nature of the hydrogen adsorbed on these catalysts. The results were used to understand the different behaviors of these catalysts in various catalytic reactions.

Microcalorimetry of hydrogen on supported metal catalysts

The design of 'better' catalysts demands an understanding of the role of catalyst surface as well as its interaction with the reactants of interest. Numerous experimental techniques are used to characterize this interaction. Some techniques probe the bulk of the catalyst while others are sensitive enough to investigate the surface characteristics. The advantages and disadvantages as well as the applications of the techniques are extensively discussed in the literature [8-10]. The experimental work is complemented with theoretical studies particularly with respect to understanding the energetics and thermodynamics of the fundamental processes occurring on the catalyst surface. In this work microcalorimetry was used to experimentally determine the heats of adsorption.

Heats of adsorption have been measured since Dewar determined the heats of adsorption of oxygen, nitrogen and hydrogen on graphite at low temperature in 1904 [11]. In spite of the importance of heats of adsorption in characterizing and understanding catalytic processes there have been few studies to determine the energetics of adsorption at high temperatures and pressures. Furthermore, there is little agreement between the heats determined by different research groups [12]. There has been a resurgence of interest in using calorimetry as a characterization technique with the development of modern high temperature calorimeters and transducers in the 1980's. One such high temperature transducer was used to construct the isoperibol, differential heat-flux microcalorimeter of the Tian-Calvet design used in the present work. The calorimeter is based on the design of Handy et al. [13]. For further details regarding the highly specialized field of calorimetry the reader is referred to reference [14]. In calorimetry both the amounts adsorbed and the heat evolved during the adsorption process are measured simultaneously. The objective of the present work is to use microcalorimetry as a tool to investigate catalytic processes.

Heterogeneous catalysis involves the chemisorption of at least one reactant, through bond formation with the atoms on the catalyst surface. A characteristic quantity of heat, called the heat of adsorption, is released during the chemisorption process. Factors which may influence heats of adsorption include the chemical nature of the gas and metal catalyst investigated, the amount of adsorbate present on the catalyst surface (coverage), temperature and pressure of adsorption, the size of the catalyst particles, the presence of additives, the nature of the support and the method used for heat determination.

Since both surface atoms and the adsorbate are involved in the bond formation process the heat of adsorption depends on the chemical nature of the catalyst surface and the adsorbing molecule. Thus, the heat of adsorption can give information on the changes resulting in the catalyst surface as well as the adsorbing gas, as a result of the adsorption process [2]. A comparison of the heats of adsorption of a given reactant on different catalysts can give information or clues regarding processes which might occur due to changes in catalyst structure and/or composition. For example, in the present study (see Chapter 1), it was concluded that there was no electronic effects on addition of alkali promoters because the initial heats of hydrogen adsorption were similar on Ru/SiO_2 and K/Ru/SiO_2.

Dissertation organization

Each of the following chapters corresponds to a paper written in a format suitable for publication in a technical journal. They represent original work carried out by the author. In Chapter 1 the work investigating the influence of K promoter on hydrogen chemisorption on Ru/SiO_2 is presented. In Chapter 2 hydrogen chemisorption on Ru/SiO_2, Ru-Ag/SiO_2 and Ru-Cu/SiO_2 has been discussed. In Chapter 3 the work investigating hydrogen adsorption on Ru, Rh and Pt is presented. The ^1H NMR work was done by Dr. N. Savargaonkar under the guidance of Dr. M. Pruski of Ames Laboratory.

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GENERAL CONCLUSIONS

The initial heats of hydrogen adsorption was unchanged on addition of K to Ru/SiO_2 suggesting that the chemisorption bond strength was not influenced by processes, such as electronic effects, on the promoted catalysts. There was a significant reduction in the stoichiometry of hydrogen adsorption and a decrease in the amount of hydrogen adsorbed on the promoted catalysts. This decrease in stoichiometry was due to the depopulation of sites characterized by intermediate and low heats of adsorption. The amount of spillover was lower on the promoted catalyst than on Ru/SiO_2 because of less weakly bound hydrogen available for spillover and also because K blocked sites on the silica support. ^1H NMR studies indicated that the rates of adsorption and desorption were diminished on the alkali promoted catalysts.. This decrease in the rates of adsorption and desorption may be responsible for the significant depopulation of weakly bound hydrogen in the presence of K promoter.

The microcalorimetric studies with Ru-Ag and Ru-Cu bimetallic systems indicated that the initial heats of hydrogen adsorption on Ru/SiO_2 was not altered as a result of adding Cu or Ag. This indicated that addition of Ag or Cu did not influence the chemisorption bond strength. The stoichiometry of hydrogen adsorption was significantly less on Ru-Cu and Ru-Ag than on Ru/SiO_2. The decrease in stoichiometry was more with Ag than with Cu because Cu, unlike Ag, accommodates spillover hydrogen initially adsorbed on Ru. The decrease in stoichiometry of adsorption was due to the depopulation of the intermediate and weak sites. Since Ag and Cu preferentially occupy the edges, corners and other low coordination metal sites, the reduced amount of weakly bound hydrogen was correlated to the availability of low metal coordination sites. The kinetics of adsorption and desorption was also altered on addition of Cu or Ag to Ru/SiO_2.

The stoichiometry of hydrogen adsorption and the amount of hydrogen adsorbed was significantly higher on Ru/SiO_2 than on Rh/SiO_2 or Pt/SiO_2. The population of intermediate and weak hydrogen adsorption states was much higher on Ru/SiO_2 than on Rh and Pt. The fraction of strongly bound hydrogen was higher on Rh/SiO_2 and Pt/SiO_2 than on Ru/SiO_2. The large amounts of weakly bound hydrogen on Ru/SiO_2 was responsible for the significant spillover seen in this catalyst system. It was postulated that the electronic structure were responsible for the unique kinetics of hydrogen adsorption observed on Ru/SiO_2. The kinetics of hydrogen adsorption and desorption were responsible for the large amounts of weakly bound hydrogen observed on Ru/SiO_2 relative to Pt and Rh.

APPENDIX. OPERATING INSTRUCTIONS FOR MICROCALORIMETER

1. Weigh approximately 0.7 to 1 gram catalyst in the sample cell and an identical amount of inert support in the reference cell. Use ultra Torr fittings to attach the sample and reference cells to the volumetric system shown in figure A.1.
2. Slowly raise the temperature of the volumetric system to 130° C.
3. Mount the furnaces around the cells and insert thermocouples.
4. Close valves NV1, B5 and B3. Open all other valves
5. Switch on mechanical pump and turbo pump.
6. Slowly open B5 followed by NV1.
7. Evacuate for 10 minutes.
8. Slowly raise temperature to 220° F and evacuate at this temperature for at least 30 minutes.
9. Gradually raise temperature to desired reduction temperature at 20° F per minute.
10. Close valve B6 and trap hydrogen at 760 Torr in the volumetric system by opening valve B1. Close valve B1.
11. After 30 minutes open valve B6 to evacuate the system.
12. Repeat steps 10 and 11 at least 5 to 6 times.
13. Note total time of reduction.
14. Open valve B6 to evacuate at reduction temperature for a time period equal to the total time of reduction.
15. Switch off the furnaces and cool to room temperature under evacuation.
16. Remove furnaces.
17. Apply a thin layer of thermal grease (Dow Corning 340) around the cells.

18. Place the cells in their respective chambers in the calorimeter by carefully raising the calorimeter block around the cells.
19. Cover the two chambers with the custom made polyimide covers.
20. Tightly pack the calorimeter opening with glass wool to insulate the cells.
21. Cool the volumetric system to room temperature.
22. Close valve NV1 and B5.
23. Open valve B1 and flush system by flowing helium through the volumetric system for 10 minutes.
24. Close valve B6, B2 and B1 to trap helium at pressure H1.
25. Open valves B5 and NV1.
26. When the pressure reading is steady note the pressure H2.
27. Close NV1 and note the pressure H2N`.
28. Open valve NV1
28. Close valve B5 and note the pressure H2B`.
29. Open valve B5.
30. Open valve B6.
31. Slowly raise temperature of calorimeter block and volumetric system to 140^{o} C.
32. Connect variac between the calorimeter controller and calorimeter heater.
33. Allow to equilibrate overnight.
34. Close valves B5 and NV1.
35. Flush volumetric system for 10 minutes with the gas being studied.
36. Trap gas in volume V1 + V2 by closing valves B2 and B6. Allow to equilibrate. Close valve B4 and note pressure P_{IKS}.
37. Start program AOP2 on the computer and follow instructions displayed on the screen. Output file name, sampling rate in milliseconds and

comments on the run are to be entered. Acquire baseline for at least two minutes. The baseline should be flat.

38. Note the temperatures on channels P1 and P2 of the RTD readout. This corresponds to the temperature, $T_{BLOCK/CELL}$, of the calorimeter cells.
39. Note the temperature T_{V1} on the controller of the volumetric system along with the temperatures T_{V2}, T_{V3} and T_{V4} of the thermocouples T2, T3 and T4.
40. Open valve B5.
41. Open needle valve NV1 continuously over at least 4 minutes.
42. After thermogram comes back to the baseline close valves NV1 and B5.
43. Stop the program AOP2.
44. Open valve B6 to evacuate volume V2. Close B6.
45. Open valve B4.
46. Note pressure P_{FKS}.
47. Open valve B6 and evacuate volume V1 and V2.
48. Repeat steps 35 to 47 for next dose at a higher initial pressure P_{IKS}.
49. Continue dosing until desired coverage or differential heat of adsorption has been obtained.
50. After the experiment is complete switch off the calorimeter heater and cool calorimeter to room temperature.
51. Weigh the sample cell with reduced catalyst.

Safety

1. Wear safety glasses, dust and mist respirator, gloves, lab coat and preferable a cap while working with glass wool. Please determine whether you are allergic to glass wool.
2. Wear heat resistant gloves while handling hot furnaces.

3. Extreme caution should be exercised while raising the calorimeter block around the glass cells. If the glass cells break during set up IMMEDIATELY close valves NV1 and B5.
4. Wash your hands and face with plenty of soap and water once the setup is complete.
5. Wash the lab coat after every setup as the coat traps glass wool particles and fibres.

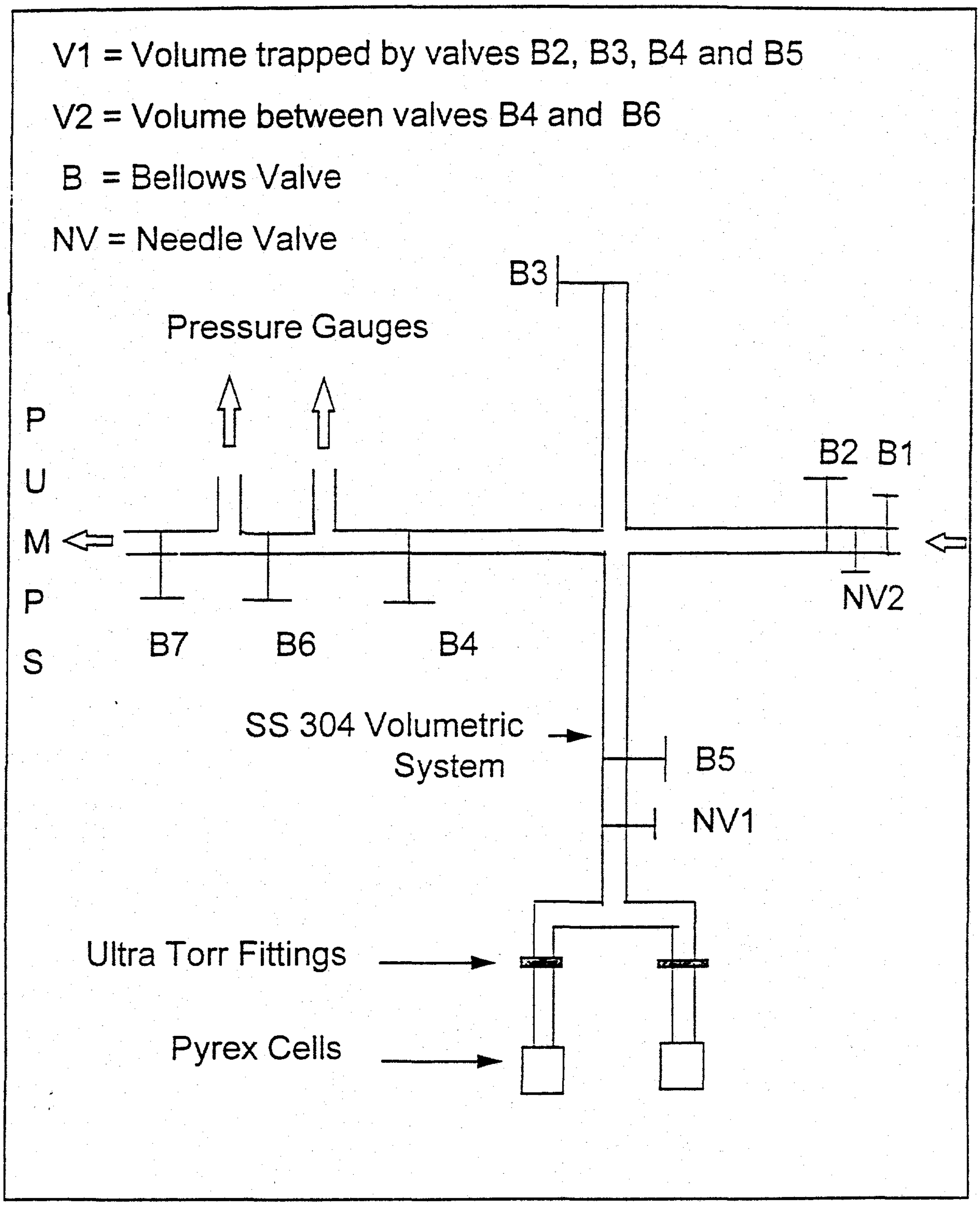

Figure A.1. Volumetric system

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