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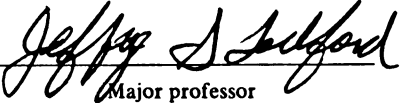
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**PREPARATION AND CHARACTERIZATION OF
VANADIUM OXIDE/ALUMINUM ANTIMONATE AND
SUPPORTED ANTIMONY OXIDE CATALYSTS**

By

Thomas John Curtis

A THESIS

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF VANADIUM OXIDE/ALUMINUM ANTIMONATE AND SUPPORTED ANTIMONY OXIDE CATALYSTS

By

Thomas John Curtis

A variety of bulk and surface characterization techniques have been used to examine the structure and reactivity of novel V/AlSbO₄, Sb/Al₂O₃, and Sb/SiO₂ catalysts. This work will establish the active phase(s) of these catalysts.

V/AlSbO₄ has been characterized using XPS, XRD, IR, solid-state NMR, and EPR. XPS V 2p_{3/2} binding energies for the catalysts indicate that V is in the +5 oxidation state. For V₂O₅ loading ≤ 20 wt.%, XPS data suggest that the V is highly dispersed over the AlSbO₄ carrier. For loading ≥ 25 wt.%, XPS indicates that V is poorly dispersed. These results are consistent with XRD and IR data obtained. Propylene oxidation data shows that vanadium promoted sample shows a greater selectivity to acrolein (90%) for 5 wt.% vanadium than to that of the pure support (59%). The increase in selectivity of propylene to acrolein is due to V=O bond.

Sb/Al₂O₃ and Sb/SiO₂ catalysts have been characterized using XPS and XRD. XPS Sb 3d_{3/2} binding energies indicate that the Sb is in the +5 oxidation state. XPS data indicates that Sb is highly dispersed over the alumina and silica supports. CO oxidation activity is highest for catalysts with active phase loadings of 10-20 wt.% Sb₂O₅ on both Al₂O₃ and SiO₂. CO oxidation activity over AlSbO₄ is greater than that measured for the Sb/Al₂O₃ catalysts.

**To my parents, Thomas and June, my sister, Denise,
and my nephews, Nicholas and Alexander**

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I would like to thank Dr. Jeffrey Ledford for his guidance and support during the course of this work and for all the knowledge I obtained in our conversations. Without his support this project would never have been accomplished. I would like to thank my parents, my sister and my nephews for their support and understanding during the past few years. I would also like to thank the Ledford group members, Jeff R., Paul, Kathy, Greg, Mike, Mark and especially Ed and Per with their help with ChemDraw and Designer. I would like to thank the rest of the graduate students, especially Tim, Scott and Doug for their friendship during this time. Finally, I would like to thank all people who have provided assistance on this project.

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Chapter 1

Introduction to Selective Oxidation Catalysis

1.1. Overview of Selective Oxidation Reactions

Selective oxidation of hydrocarbons is an important industrial process that uses transition metal oxide catalysts to convert less valuable hydrocarbons into more valuable compounds (e.g., acrolein and acrylonitrile). The most common catalysts used for these processes are based on metal oxides of vanadium and molybdenum. A common feature of these reactions is that the desired products are often not the most thermodynamically favorable ones. For reactions carried out in either air or oxygen, the most thermodynamically favored products are water and carbon dioxide. The desired products are alcohols, aldehydes, ketones, acids, anhydrides, or alkenes and dienes [1]. Thus, for each hydrocarbon, numerous products of various extents of oxidation are formed before carbon oxides are produced. Hence, it is a challenge to understand the factors that account for the selectivity and activity of a catalyst and to develop a practical catalyst. In selective oxidation reactions, the selectivity is usually dictated by the ability of the metal oxide to catalyze the formation of C-O bonds while minimizing the breaking of C-C bonds.

Selective oxidation reactions can be classified into two types: dehydrogenation and dehydrogenation followed by oxygen or ammonia insertion. In dehydrogenation reactions, aliphatic molecules are converted into alkenes by breaking C-H bonds and forming C=C bonds. Often oxygen is used as an oxidant to yield water as a byproduct. The oxygen additionally provides the thermodynamic driving force for this process. Other oxidants (e.g., I, Br, and N₂O) can be used, but oxygen allows the reaction to be conducted at lower temperatures [1].

In dehydrogenation and oxygen insertion processes, C-H bonds are broken and C-O bonds are formed. Oxygen is used as an oxidant for the formation of oxygenates and in the formation of water in the dehydrogenation step. Exceptions to this general rule are the oxidation of ethylene to ethylene oxide in which no C-H bonds are broken and ammoxidation reactions (such as propylene to acrylonitrile) in which C-N bonds are formed. Oxidation of benzene to maleic anhydride is an example of a reaction that involves the breaking of C-C bonds and the insertion of oxygen.

Catalysts used for selective oxidation and ammoxidation reactions contain several types of sites: olefin chemisorption sites, α -hydrogen abstraction functions, oxygen or NH insertion sites, and redox couples associated with dioxygen dissociation. The olefin chemisorption site and the oxygen or NH insertion sites are often associated with elements in their highest oxidation state (e.g., Mo^{+6} or Sb^{+5}). The α -hydrogen abstraction site consists of metalloids with free electron pairs (e.g., Bi^{+3} or Sb^{+3}) that give radical character to the oxygen bond at the site. The presence of radical oxygen facilitates the abstraction of α -hydrogen as a radical from the chemisorbed olefin (an important step in the formation of the π -allyl intermediate). Oxygen or NH insertion from maximum valency metal sites into the π -allyl species and forms the σ -allyl surface intermediate. During this process, reduction of the metal (e.g., Mo^{+6} to Mo^{+4} in molybdate catalysts) occurs followed by desorption of the product. A redox couple with a reduction potential greater than that of the oxygen or NH insertion site may also be present to facilitate reoxidation of these elements back to their original active state. The redox element also serves as a site for O_2 reduction [2]. Figure 1.1 shows the general reaction mechanism for the selective oxidation of propylene.

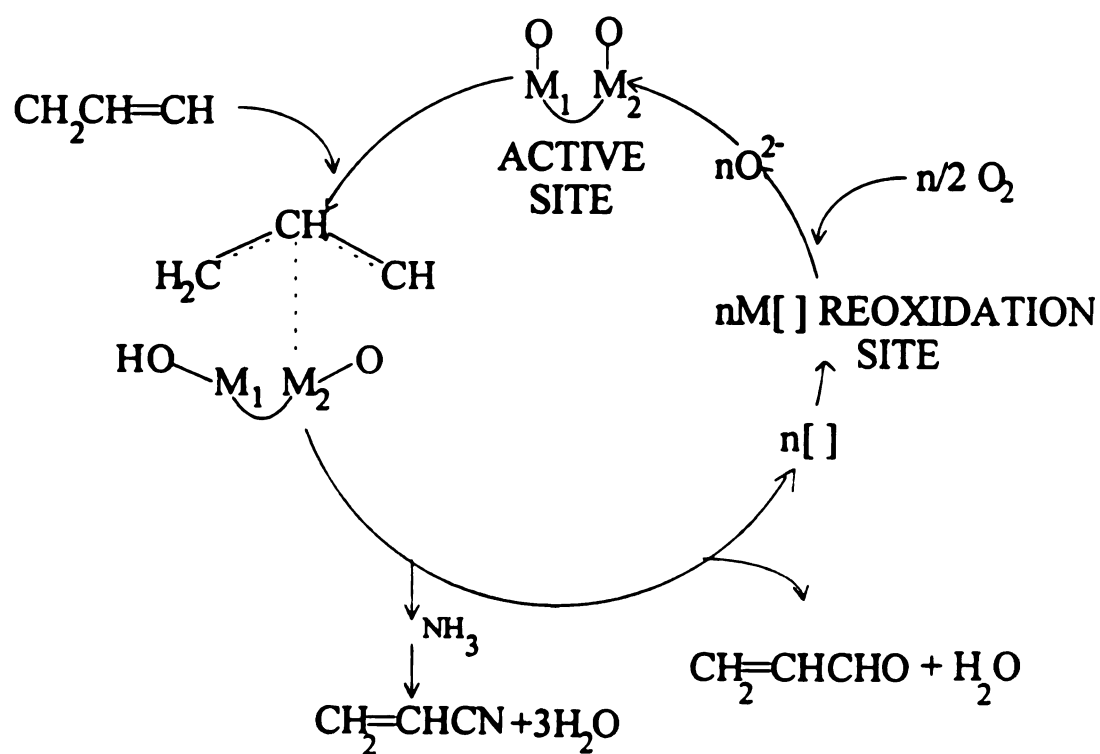
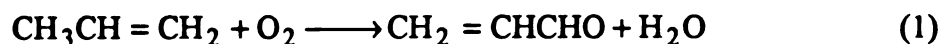
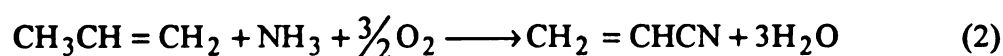


Figure 1.1. Reaction mechanism for selective oxidation and ammoxidation of propylene.

Among the most commercially important examples of selective oxidation are the oxidation of propylene to acrolein:



and ammoxidation of propylene to acrylonitrile:



which are used for further reactions with hydrocarbons to produce valuable compounds.

In 1948, Adams used cuprous oxide as the catalyst to transform propylene into acrolein, with a yield of approximately 50% [3]. In 1959, Idol improved the yield of propylene oxidation to acrolein by using a bismuth-molybdate catalyst [4,5]. The bismuth-molybdate catalyst was also found to convert a reactant mixture of propylene, air, and ammonia to acrylonitrile [6]. Commercial vapor-phase oxidation and ammoxidation was developed by Standard Oil of Ohio (SOHIO). In 1965, Adams [7] found that the bismuth-molybdate catalyst could produce butadiene from butene. Also, in 1965, a more selective uranium-antimony catalyst was introduced for the same set of reactions. In order to eliminate the radiation concerns associated with the use of uranium, an iron-antimony catalyst was developed. This catalyst is still used in Japan [8-11].

In 1970, SOHIO introduced the first multicomponent catalysts [12,13]. These catalysts were composed of a variety of elements including Bi and Mo. Based on research by various workers, Burrington et al. [14] proposed detailed mechanisms for both oxidation and ammoxidation over bismuth molybdate. The mechanisms for oxidation and ammoxidation are shown in Figure 1.2.

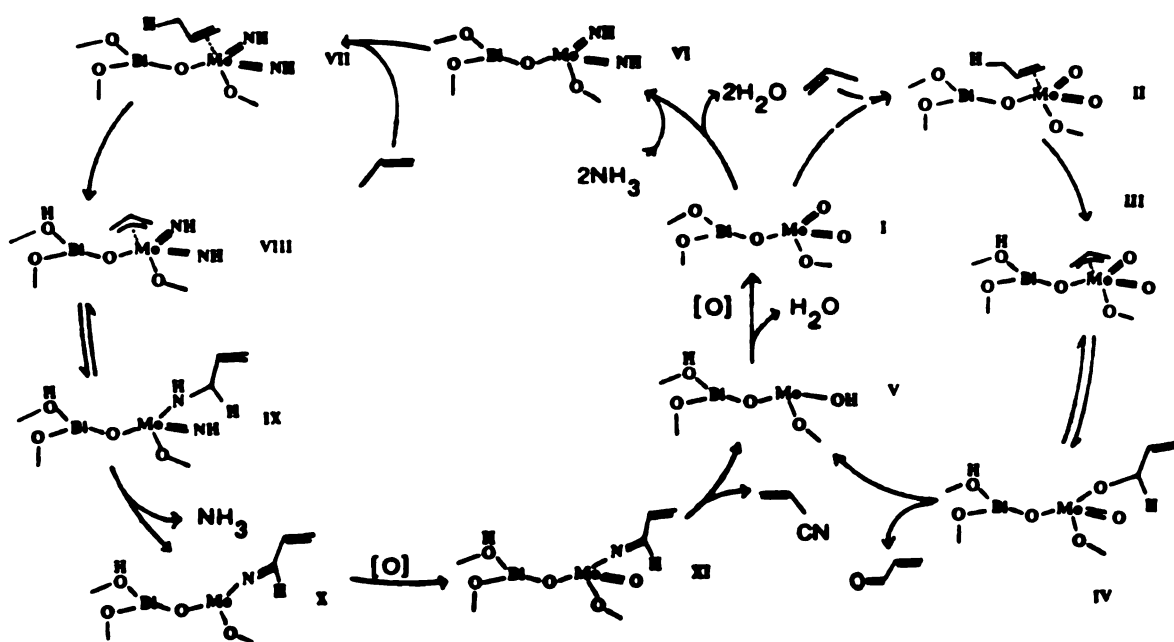


Figure 1.2. Mechanism of selective ammoxidation (left) and oxidation (right) over bismuth molybdate. (From *J. Catal.*, **87**, 373, 1984).

In these mechanisms, the surface active site is a Bi-Mo pair site that is composed of a Bi-O group responsible for allylic H abstraction and a molybdenum dioxo group for nitrogen insertion. It is believed that propylene absorption occurs at the molybdenum cation. The oxidation reaction proceeds by dissociative adsorption of propylene to produce a π -allyl species. It is not clear, at present, whether dissociation of propylene occurs upon adsorption or propylene is first adsorbed molecularly as a π complex and allylic H abstraction follows. The next step is the formation of C-O bonds and a second hydrogen abstraction in the form of a (1,4) shift to produce adsorbed acrolein and Mo-OH. Finally, the product desorbs and the catalyst is reoxidized.

In ammoxidation, a surface molybdenum diimido species is formed by the reaction of dioxo groups with ammonia. The activation of the propylene occurs in the same manner as the oxidation cycle. The reaction proceeds by dissociative adsorption of propylene, followed by formation of a C-N bond and two additional hydrogen abstractions producing acrylonitrile. The reduced surface site is reoxidized and then reconverted to the diimido species.

Because of the reduced cost and the greater availability of alkane feedstock, significant effort has been devoted to understanding the reaction mechanism for the oxidation and ammoxidation of propane. At present, Cantani et al. [15] suggest that the reaction mechanism occurs as shown in Figure 1.3. In this scheme, the propane is converted to the main product of propylene, which then further reacts to form acrylonitrile (ACN), acetonitrile (AcCN), hydrogen cyanide (HCN), ethane and ethylene (C₂), and carbon oxides (CO_x). They suggest that the formation of acrylonitrile passes through the intermediate formation of propylene and the production of acrylonitrile is limited by the slow rate of propylene formation.

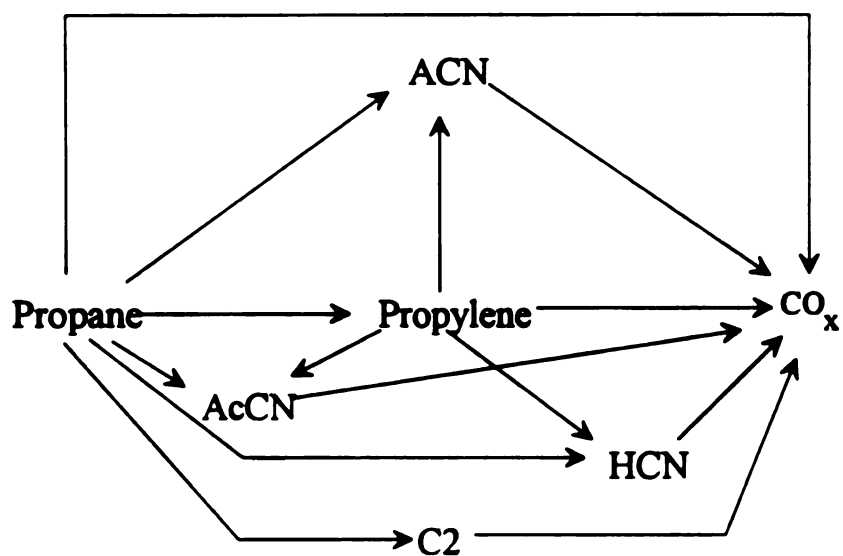
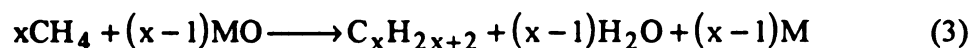


Figure 1.3. Reaction mechanism for selective oxidation and ammoxidation of propane.
(From *Ind. Eng. Chem. Res.*, 31, 107, 1992).

1.2. Overview of Methane Conversion

Recently, there has been increased interest in the oxidative coupling of hydrocarbons primarily using metal oxide, rare earth oxide, alkaline earth oxide and alkali metal-doped oxide catalysts. The oxidative coupling of methane to form ethylene and ethane has received considerable attention due to the abundance and low cost of methane. Interest in oxidative coupling has also increased due to the possibility of conversion to either gasoline, distillate or other products. The conversion over metal oxides is thought to occur as follows:



In 1969, Union Carbide investigated the feasibility of using methane coupling for ethylene manufacturing [16]. They performed extensive studies on different metal oxides for this process and found that most of the metal oxides of group IIIA, IVA, and VA exhibit both high activity and selectivity for methane coupling. In 1979, Mitchell and Wagborne of Exxon [17] achieved 40-50% conversion of methane to mainly ethane and ethylene over a catalyst consisting of a group VIII noble metal, a group VIB metal oxide, and a group IIA metal. Between 1983 and 1986, Baerns et al. [18] studied several lead oxide supported on γ -alumina, silica, and alumina/silica catalysts. Their work showed low acidity supports are preferred for high selectivity to C_2 's. From 1984-1987, Arco [19] screened a large number of metal oxides supported on silica. They reported that manganese, indium, germanium, antimony, tin, bismuth, and lead oxides achieved approximately 15% conversion and give 10-50% selectivity to higher hydrocarbons. They also found that more acidic catalysts were less selective to C_2 formation. Further, they reported that addition of alkali metal leads to an increase in C_2 's selectivity [20,21].

Both reducible and irreducible oxides have been used for methane coupling. Bhasin and Keller [22] found that oxides of Sn, Pb, Sb, Bi, Tl, Cd, and Mn were the most active. They performed the reaction without the addition of O_2 in the gas stream. They concluded that the common characteristic of the active metals was that they could cycle between at least two oxidation states. Thus, these reactions can be considered as oxide reduction.

A number of irreducible metal oxides (e.g., MgO, Li/MgO, Na/CaO, Sr/La₂O₃, and Li/TiO₂) have been studied as methane coupling catalysts [23-26]. In these systems, oxygen in the gas stream is required to generate and maintain activity, but the oxidation state of the metal oxide does not change. These catalysts also have an advantage over the reducible catalyst because they are easier to control.

The oxidative coupling reaction mechanism and the nature of catalytic coupling site over Li/MgO has been extensively studied by Lunsford et al. [27]. Oxidative coupling is proposed to proceed via the abstraction of hydrogen by lattice oxygen from the metal oxide followed by gas-phase coupling of methyl radicals. The methyl radicals can then combine to form ethane or react with oxygen to form products as shown in Figure 1.4. The pathway leading to complete oxidation is more complex. High selectivity to CO₂ is observed when the reaction is conducted in the presence of O₂. This suggests a significant gas-phase contribution to CO_x production, possibly by methylperoxy radicals or adsorbed oxygen. In addition, a surface assisted route evident during the initial phases of the reaction in the absence of O₂ can contribute to CO_x production [28].

In addition to methane coupling, ethane, and propane coupling have received considerable attention. Recently, Otsuka et al. [29] showed that at temperatures less than 650 K, Na₂O₂ partially oxidizes methane, ethane, and propane to ethane, butane, and hexane, respectively. Kinetic studies by Otsuka suggests that the activation of methane is initiated by diatomic oxygen such as O₂⁻, O₂⁻² or O₂ which are adsorbed on the

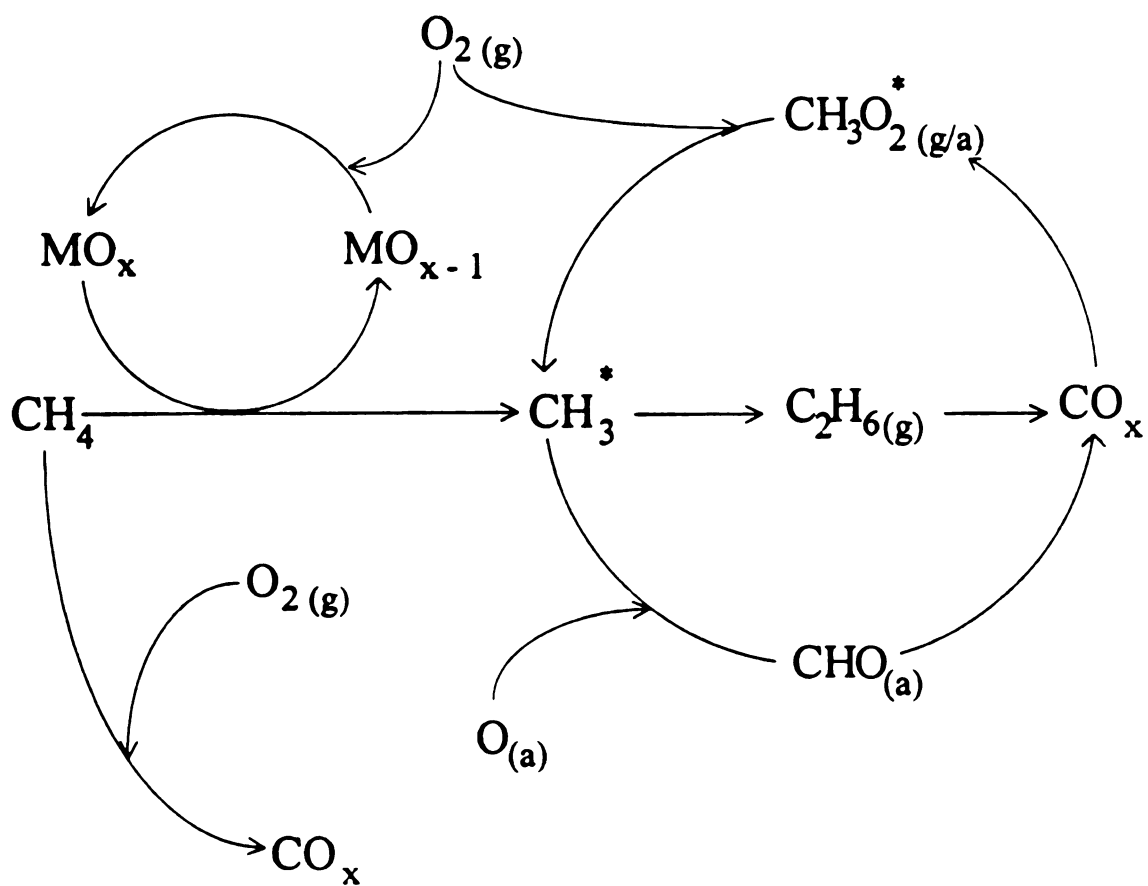
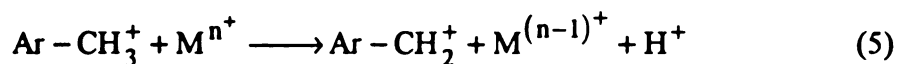
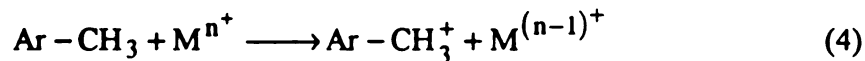


Figure 1.4. Reaction mechanism for methane conversion. (From *J. Catal.*, 112, 168, 1988).

surface [30,31]. The proposed mechanism for these reactions is shown in Figure 1.5.

In addition to the coupling of aliphatic hydrocarbons, there is interest in the coupling of aromatic hydrocarbons such as methylbenzenes. The catalytic oxidation of methylbenzenes by metal oxides to the corresponding aldehyde and acid are well known industrial processes [32]. In a recent patent [33], anthraquinone was reported to be the major product of the oxidation of methylbenzene. King [34] recently found that under anaerobic conditions methyl-aryl coupling reactions occurred to produce methyldiphenylmethanes from the methyl-substituted benzenes. The corresponding aldehydes and acids were minor products. From this work, King concluded that methyl-aryl coupling is more favorable using more basic and ionic metal oxides formed from elements on the left side of the periodic table. A possible explanation for this finding is that a methylbenzene molecule may be polarized on the oxide and a proton from the methyl group abstracted to form OH^- on the surface. If the multivalent metal oxidant (M^{+n}) is easily reducible, the benzyl anion may transfer two electrons to form a benzyl cation. The overall reaction involves reduction of the metal oxide and formation of water from OH^- and H^+ . The reaction is believed to occur by the following mechanism:



For easily reducible metal oxides, the reaction occurs through the methylene group on the methylbenzenes. The first step of methylbenzene oxidation on the oxide is believed to involve the abstraction of α -hydrogen to form water. The oxide at the surface may be reduced to its metallic form which has very weak interaction with the adsorbed organic

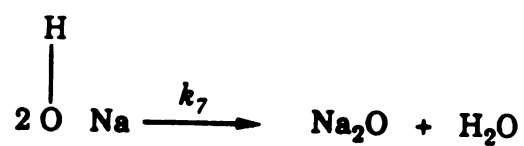
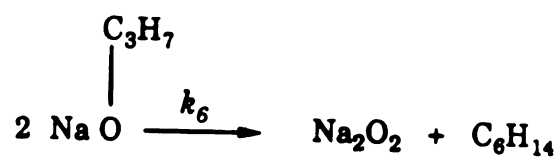
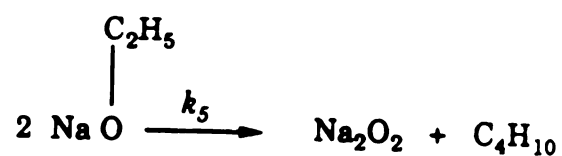
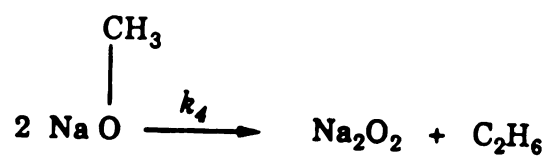
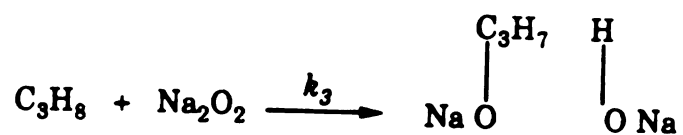
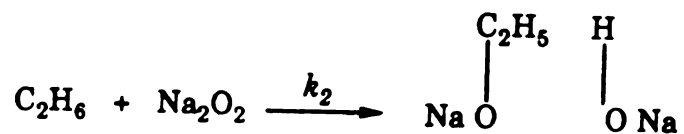
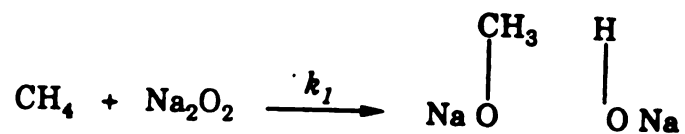


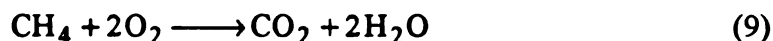
Figure 1.5. Reaction mechanism for non-catalytic coupling of methane. (From *J. Catal.*, 121, 122, 1990).

species. A proposed mechanism on PbO is as follows:



The formation of bibenzyl occurs through methyl-methyl coupling.

In addition to oxidative coupling of methane to higher hydrocarbons, the deep oxidation of CH_4 to CO_2 has potential for large scale application. Deep oxidation of methane was widely studied in the 1960's and 1970's when it was hoped that less costly alternatives to $\text{Pt}/\text{Al}_2\text{O}_3$ total combustion catalysts could be found [35]. The use of catalysts for total oxidation of hydrocarbons offers several advantages over more conventional destruction methods such as thermal incineration. For example, the formation of carbon and nitrogen oxides can be completely prevented by using appropriate catalyst formulations. The deep oxidation of methane is described by the following reaction:

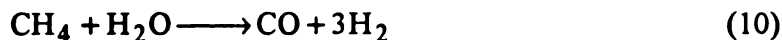


In addition to $\text{Pt}/\text{Al}_2\text{O}_3$, other catalysts such as Pd, Rh, and first row transition metal oxides have been used for this reaction [36].

Recently, Lacombe et al. [37] have studied the total oxidation of methane pathway in oxidative coupling of methane over lanthanum oxide catalysts. They found that total oxidation into CO_2 proceeds mainly through surface reactions by slow steps which combine with the initial slow step of methane activation.

In addition to methane coupling and total oxidation, partial oxidation of methane to CO and hydrogen has received considerable attention. Among the most important

commercial methods of synthesis gas manufacturing is the steam reforming of natural gas and light hydrocarbons. For methane, the reaction is as follows [38]:



Typical catalyst used are CaO and/or K₂O promoted Ni/ α -alumina, MgO or MgAl₂O₄. Prettre et al. [39] were among the first to study synthesis gas formation by catalytic conversion of CH₄/O₂ mixtures with 10 wt.% nickel/refractory oxide catalyst. They found that the compositions of the final CH₄/CO/CO₂/H₂ reaction mixture agreed with thermodynamic predictions.

1.3. Overview of CO Oxidation

In recent years, there has been increased interest in the environment and the effect of technology on the environment. Air pollution is generated from emission sources such as electric power generation, refuse burning, industrial, and domestic fuel burning, industrial processes and transportation. CO is the most abundant air pollutant in the lower atmosphere.

CO oxidation was first studied by Langmuir [40] in 1922 over group VIII metals. In general, the reaction occurs as follows:



Even though the overall reaction is very simple, the reaction kinetics are, in fact, rather complicated. For example, when performed on Pd, the rate dependencies of the reaction vary from negative first order to positive first order for each reactant [41,42]. In addition,

surface diffusion of adsorbed CO [43,44] and metal surface restructuring under reaction conditions [45] also complicate the interpretation of kinetics data. CO oxidation has been extensively studied on single-crystal Pd and supported Pd crystallites. Evidence suggests a surface reaction between an adsorbed CO molecule and an oxygen atom occurs.

Most commercially employed catalysts for CO oxidation utilize noble metals. This is because they have high intrinsic activity for oxidation, are not greatly deactivated by sulfur in fuel at temperatures $< 500^{\circ}\text{C}$, and have good thermal stability. However, at temperatures between $500\text{--}900^{\circ}\text{C}$, the pure metal sinters rapidly. Furthermore, it has been found that the noble metal can disperse as oxides on supports at temperatures below the decomposition temperature of the oxides [51].

Although noble metal catalysts are more developed, base metal oxide catalysts are of importance because of the natural abundance and lower cost. Frontier research in this area focuses on the development of contaminant resistant and thermally stable base metal oxide catalysts for catalytic combustion [52].

In 1923, Jones and Taylor reported that copper is an active catalyst for the reaction between CO and O_2 [47]. Ertl [48], Harbraken et al. [49], and Arlow and Woodruff [50] have performed studies on Cu single-crystals and found that high oxygen coverage retards the reaction rate and that a surface reaction between an adsorbed CO molecule and an oxygen atom occurs. However, there is no agreement as to structural sensitivity of the reaction. Since oxygen adsorbs more strongly than CO on Cu, high oxygen coverage usually exists and reactions rates are lower. Thus, copper oxide requires higher temperatures to obtain similar activities per unit surface area in comparison with noble metal catalysts. Prokopowicz et al. [53] have studied CO oxidation over CuO/SiO_2 and observed first-order dependency on CO (characteristic of base metals) and zero-order on O_2 above 4% O_2 . Huang et al. [54] have reported a strong dependence of

pretreatment on the activity of CO oxidation on CuO/ γ -Al₂O₃ catalysts and concluded the reaction is structure sensitive.

In general, high oxidation activity requires metal ions that can have more than one valence state and can participate in redox reactions. Among the most promising oxides are Co₃O₄, NiO, Cr₂O₃, and CuO because they are refractory oxides and thus maintain their activity at high temperature. Mixtures of these oxides often exhibit greater stability and activity than the single oxide. One such mixture that has been shown to have activity near that of noble metal catalysts is the copper-chromium catalyst. In this system, it has been suggested that copper oxide is the active component and chromium oxide is a promoter.

1.4. Focus of Research

1.4.1. Selective Oxidation

The discovery of selective oxidation and ammoxidation of alkenes has been the subject of much commercial interest. Recent research effort has focused on the development of selective oxidation and ammoxidation catalysts for the activation of less expensive feedstocks, such as propane and methane. The catalysts commonly used are prepared by mixing a hydrosol or gel of the carrier with a slurry of a solution containing the active phase(s) and the promoters such as W and/or Mo. This procedure can produce very complicated catalyst structures which makes comprehensive characterization difficult. Thus, the effect of surface structure on the properties of the catalyst and the active sites are not well known. In order to understand the influence of the catalyst structure on hydrocarbon activation, a simple catalytic system must be examined.

Several authors have reported that vanadium antimonate catalysts are promising systems for the ammoxidation of propylene [55] and propane [56] to acrylonitrile. Centi et al. [57] have investigated the structure and activity for selective oxidation and ammoxidation of propane for VSbO_x mixed oxides supported on SiO_2 , Al_2O_3 , and TiO_2 and promoted with W or Mo. Their work suggests that VSbO_x phase plus Sb_2O_5 is not the active phase for ammoxidation. They proposed that the random rutile phase of AlSbO_4 (Figure 1.6) modified with vanadium is the active phase for the formation of propylene and vanadium or other redox elements having $\text{M}=\text{O}$ bonds (W or Mo) is needed to form acrolein or acrylonitrile. Although $\text{VSbO}_x/\text{Al}_2\text{O}_3$ is not as complex as the commercial catalysts, further understanding of hydrocarbon activation would be obtained by studying the interaction of the pure phases believed to be responsible for selective oxidation and ammoxidation.

The objective of this work is to study mixed oxide systems which model specific active phase-support phase interactions that have been proposed to play a role in selective oxidation. The work will focus on V oxide supported on aluminum antimonate. The nature of the V- AlSbO_4 interaction as well as the influence of V dispersion and reactivity on the catalytic properties of the mixed oxide will be determined.

1.4.2. Methane and CO Oxidation

The surface catalyzed coupling of methane has had limited success mainly because direct coupling of methane is a thermodynamically forbidden process at the reaction conditions of interest. However, if an oxidizing agent is used in the gas stream, either partial oxidation to methanol or oxidative coupling can take place. A number of researchers [58-62] have shown that it is possible to convert methane to higher hydrocarbons by reaction with metal oxides, thus coupling the methane through the

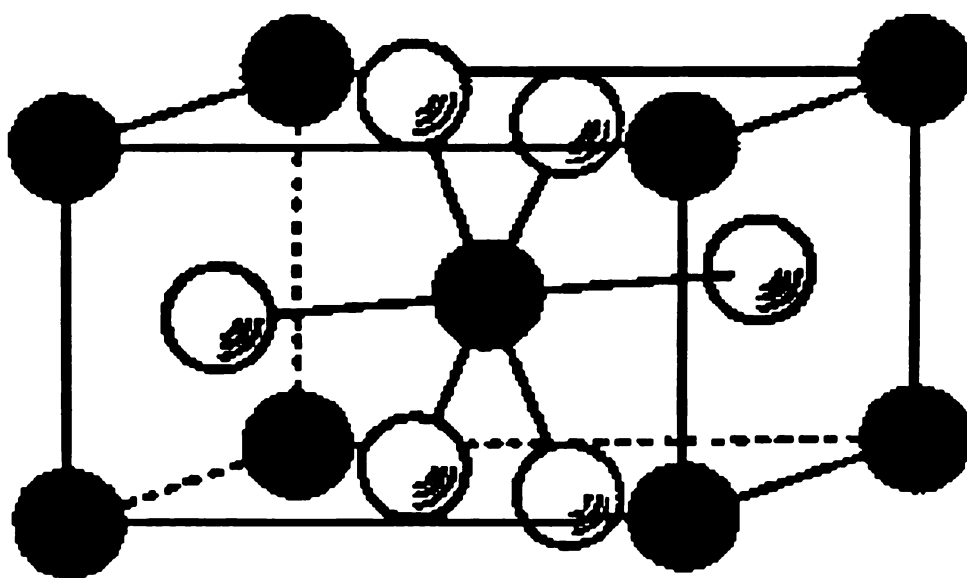


Figure 1.6. Random rutile structure. (From *Acta Chem. Scand. A*, 29(9), 804, 1975).

abstraction of lattice oxygen and the formation of water.

Antimony oxide has been used for methane coupling because the melting point of the compound lies in the low melting region of the periodic table and has been reported to give high C_2 selectivity. In addition, Sb_2O_4 is a well known allylic oxidation catalyst promoter in propylene oxidation [63].

In addition to methane conversion, antimony oxide has also been used as a promoter for the oxidation of CO [64]. Ali-Zade et al. [65] found that the activity of Cu, Co, Cr, and Mn oxides supported on γ -alumina is improved when Sb oxide is added. Antimony oxides have also been used in conjunction with oxides of Be, Mg, Zn, Al, Si and rare earth metals [66] and Sn-Mn-Pb oxides [67] for treatment of exhaust gases.

The goal of this research is to investigate the surface structure and catalytic properties of antimony catalysts supported on Al_2O_3 and SiO_2 . This work will focus on catalyst preparation and characterization and will establish correlation between activity and structural information obtained from bulk and surface spectroscopies. CO oxidation will be used as a probe reaction to obtain information about the nature of active site(s) for the reaction.

References

1. H.H. Kung, "Transition Metal Oxides: Surface Chemistry and Catalysis," Elsevier, Amsterdam, 1989.
2. J.D. Burrington, C.T. Hartisch, and R.K. Grasselli, *J. Catal.*, **81**, 489, 1983.
3. G.W. Hearn and M.L. Adams, U.S. Patent 2,451,485, 1948.
4. J.D. Idol Jr., U.S. Patent 2,904,580, 1959.
5. F. Veatch, J.L. Callahan, E.C. Milberger, and R.W. Foreman, "Proceedings, 2nd Int. Congr. Catal.," **1**, 2647, Technip, Paris, 1960.
6. F. Veatch, J.L. Callahan, and E.C. Milberger, *Chem. Eng. Process.*, **5b**, 65, 1960.
7. C.R. Adams, "Proceedings, 3rd Int. Congr. Catal.," **1**, 240, Amsterdam, 1965.
8. J.L. Callahan and B. Sertisser, U.S. Patent 3,198,750, 1965.
9. G.K. Boreskov, S.A. Ven'yaminov, A. Dzis'ko, D.V. Tarasova, V.M. Dindoin, N.W. Sazanova, J.P. Olen'kova, and L.M. Kefeli, *Kinet. Katal.*, **10**, 1109, 1969.

10. T. Yoshino, S. Saito, J. Ishikara, T. Sasaki, and K. Sofugawa, Japanese Patent 7,102,802, 1971.
11. T. Yoshino, S. Saito, and B. Sobukawa, Japanese Patent 7,103,438, 1971.
12. R.K. Grasselli, G.H. Heights, and J.L. Callahan, U.S. Patent 3,414,631, 1968.
13. R.K. Grasselli, G.H. Heights, and H.F. Hardman, U.S. Patent 3,642,930, 1972.
14. J.D. Burrington, C.T. Hartisch, and R.K. Grasselli, *J. Catal.*, **87**, 363, 1984.
15. R. Cantani, G. Centi, and F. Trifirò, *Ind. Eng. Chem. Res.*, **31**, 107, 1992.
16. M.M. Bhasin, "Methane Conversion," Elsevier Science Publishers, Amsterdam, p. 343, 1988.
17. H.L. Mitchell III and R.H. Waghorse, U.S. Patent 4,172,810, 1979.
18. W. Bytyn and M. Baerns, *Appl. Catal.*, **28**, 199, 1986.
19. J.A. Sokfranko, J.J. Leonard, and C.A. Jones, *J. Catal.*, **103**, 302, 1987.
20. C.A. Jones, J.J. Leonard, and J.A. Sokfranko, *J. Catal.*, **103**, 311, 1987.
21. J.A. Sokfranko, J.J. Leonard, and C.A. Jones, *Energy and Fuels*, **1**, 12, 1987.
22. G.E. Keller and M.M. Bhasin, *J. Catal.*, **73**, 9, 1982.
23. K.D. Campbell and J.H. Lunsford, *J. Phys. Chem.*, **92**, 5792, 1988.
24. Y. Chen, H.T. Tohver, J. Narayan, and M.M. Abraham, *J. Phys. Chem.*, **16**(12), 5535, 1977.
25. C-H. Chen, J-X. Wang, and J.H. Lunsford, *J. Catal.*, **111**, 302, 1988.
26. J.M. DeBoy and R.F. Hicks, *J. Catal.*, **113**, 517, 1988.
27. CH.H Lin, K.D. Campbell, and J.H. Lunsford, *J. Phys. Chem.*, **90**, 534, 1986.
28. M.-Y. Lo, S.K. Agarwal, and G. Marcelin, *J. Catal.*, **112**, 168, 1988.
29. K. Otsuka, Y. Murakami, Y. Wada, A.A. Said, and A. Morikawa, *J. Catal.*, **121**, 122, 1990.
30. K. Ostuka and K. Jinno, *Inorg. Chim. Acta*, **121**, 237, 1986.
31. K. Ostuka, A.A. Said, K. Jinno, and T. Komatsu, *Chem. Lett.*, **77**, 1987.
32. Kirk-Othmer, "Encyclopedia of Chemical Technology," 3rd. ed., **3**, p. 738, Wiley, New York, 1978.
33. K. Kojo, Japanese Patent 1,883,121,238, 1983.
34. S.T. King, *J. Catal.*, **131**, 215, 1991.
35. Catalysts for the Control of Automotive Pollutants: Advances in Chemistry Series 143; J.D. Mc Evory, ed.; American Chemical Society: Washington, DC, 1974.
36. E.H. Foules, J.H. Labinger, J.L. Beauchamp, and B. Fulty, *J. Phys. Chem.*, **95**, 7393, 1991.
37. S. Lacombe, J.G. Sanchez, M.P. Delidore, H. Mozzanega, J.M. Tatibouet, and C. Mirodatos, *Catal. Today*, **13**, 273, 1992.
38. D. Dissanayake, M.P. Rosynek, K.C.C. Kharas, and J.H. Lunsford, *J. Catal.*, **132**, 117, 1991.
39. M. Prettre, C. Eichner, and M. Perrin, *Trans. Faraday Soc.*, **43**, 335, 1946.
40. I. Langmuir, *Trans. Faraday Soc.*, **17**, 672, 1922.
41. T. Engel and G. Ertl, *J. Phys. Chem.*, **69**, 1267, 1978.
42. P.J. Berlowitz, H.F. Peden, and D.W. Goodman, *J. Phys. Chem.*, **92**, 521, 1988.
43. W.H. Weinberg, C.M. Comrie, and R.M. Lambert, *J. Catal.*, **41**, 493, 1976.
44. B. Mantolin and E. Gillet, *Surf. Sci.*, **166**, L115, 1986.

45. I. Keverekidis, L.D. Schmidt, and R. Aris, *Surf. Sci.*, **137**, 151, 1984.
46. H.A. Jones and H.S. Taylor, *J. Phys. Chem.*, **27**, 623, 1923.
47. G. Ertl, *Surf. Sci.*, **7**, 309, 1967.
48. F.P.H.M. Habraken, E. P. Keifer, and G.A. Bootsma, *Surf. Sci.*, **83**, 45, 1979.
49. F.P.H.M. Habraken, C.M.A.M. Mestera, and G.A. Bootsma, *Surf. Sci.*, **97**, 264, 1980.
50. J.S. Arlow and D.P. Woodruff, *Surf. Sci.*, **180**, 89, 1987.
51. J.R. Prasad, L.A. Kennedy, and A.E. Ruckenstein, *Catal. Rev. Sci. Eng.*, **26**, 1, 1984.
52. B.L. Yang, S.F. Chan, W.S. Chang, and Y.Z. Chen, *J. Catal.*, **130**, 52, 1991.
53. R.A. Prokopowicz, P.L. Silveston, R.R. Hudgins, and D.E. Irish, *React. Kinet. Catal. Lett.*, **37**, 63, 1988.
54. T-J. Huang, T-C. Yu, and S-H. Chang, *Appl. Catal.*, **52**, 157, 1989.
55. F.J. Berry and M.E. Brett, *J. Catal.*, **88**, 232, 1984.
56. G. Centi, D. Pesheva, and F. Trifirò, *Appl. Catal.*, **33**, 343, 1982.
57. G. Centi, R.K. Grasselli, E. Patane, and F. Trifirò, "New Developments in Selective Oxidation," *Stud. Surf. Sci. Catal.*, **55**, 515, 1990.
58. G.E. Keller and M.M. Bhasin, *J. Catal.*, **73**, 9, 1982.
59. I.T. Ali Emesh and Y. Amenaniya, *J. Phys. Chem.*, **90**, 4785, 1986.
60. W. Hinsen, W. Bytyn, and M. Baerns, "Proceedings 8th Intr. Congr. Catal., Berlin, 1984," **3**, p.581, Dechema, Frankfurt-am-Maion, 1984.
61. J. Driscoll, W. Martin, J.X. Wang, and J.H. Lunsford, *J. Amer. Chem. Soc.*, **107**, 58, 1985.
62. T. Ito and J.H. Lunsford, *Nature(London)*, **314**, 721, 1985.
63. V. Fattore, Z.A. Fuhrman, G. Manara, and B.J. Notari, *J. Catal.*, **37**, 215, 1975.
64. I.L. Mikhailova, I.S. Sazonova, N.P. Keier, and T.V. Belodtseva, *Kinet. Katal.*, **9**(3), 565, 1968.
65. F.M. Ali-Zade, N.M. Mardanova, P.M. Sorgin, R.M. Talshinskii, A.A. Medzhidov, and R.G. Rizaev, U.S.S.R. Patent 49,052,169, 1991.
66. S. Blumrich, R. Brand, B. Engler, W. Honnen, and E. Koberstein, European Patent 410,440, 1991.
67. Y. Ohno and K. Morishita, Japanese Patent 49,052,169, 1974.

Chapter 2

Preparation and Characterization of Mixed Metal Oxide Catalysts

2.1. Preparation of Catalysts

Recent advances in the preparation of catalysts illustrate the importance of carrier, impregnation technique, calcination temperature, and activation treatment on the structure and properties of heterogeneous catalysts [1-3]. A number of different types of interactions between an active metal oxide and the support are possible (Figure 2.1). Among them are the weak interaction between the supported oxide and the carrier, aggregates of deposited oxide electronically interacting with the carrier, metal oxide monolayers, covalently or ionically bound aggregates, solid solution of the active phase in the support, and new surface compounds. The objective of this research is to employ sophisticated synthetic procedures to control catalyst structure, thoroughly characterize the surface and bulk of the catalyst, and correlate catalyst structure with catalytic properties.

The term *impregnation* generally refers to a procedure whereby a certain volume of solution containing a compound of the active element is contacted with a high surface area support. The most common methods of impregnation include wet impregnation, incipient wetness, grafting, chemical vapor deposition, and co-precipitation.

Wet impregnation usually involves contacting a porous carrier with a solution of the active element to produce a suspension. The suspension is dried and the catalyst is activated by converting the dried phase to its active form through various physical and chemical changes (e.g., oxidation or reduction). Incipient wetness involves impregnation of the carrier with a solution whose volume corresponds to the total pore volume of the

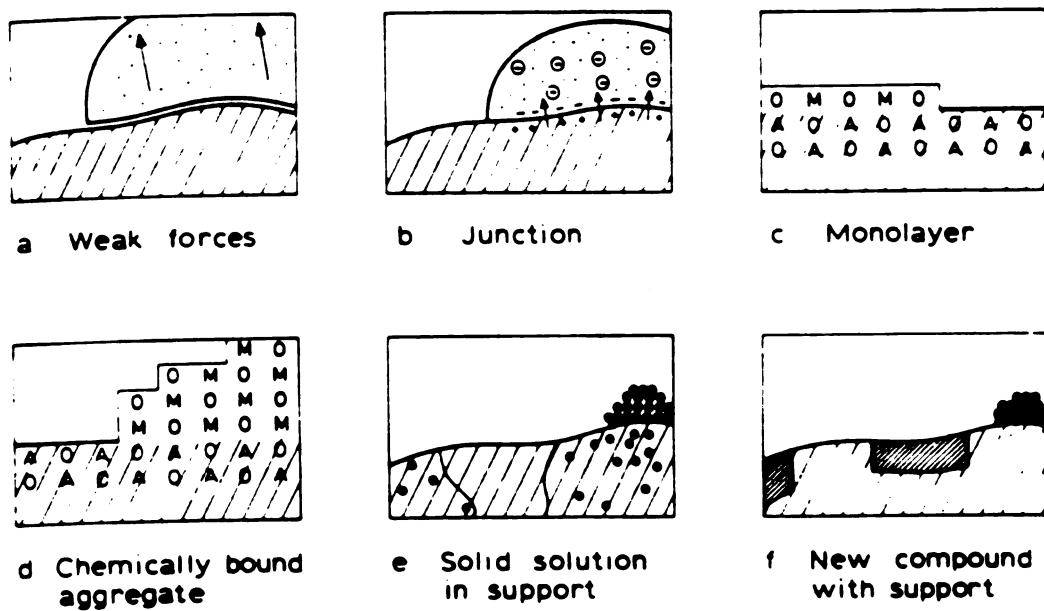


Figure 2.1. Various types of active oxide-support interaction. (From Preparation of Catalysts II, 439, 1979).

carrier [8]. The loading of the active element is controlled by varying the concentration of the impregnating solution.

Chemical vapor deposition (CVD) involves the use of volatile inorganic or organometallic compounds to prepare the catalyst. This method has been found to produce well-dispersed active components on a variety of carriers [4-7].

The active and supporting oxides or their precursors may be co-precipitated from a solution containing compounds of each element [8]. This usually produces an intimate mixing of the active phase and the support. From this close proximity with the support, the active phase is dispersed throughout the bulk as well as the surface of the catalyst. Other less involved methods of impregnation include heating a physical mixture of the oxides to induce spreading of the active phase over the supporting oxide [9].

Recently, grafting reactions have been used to obtain monolayers of various active phases [10]. This preparation method involves a chemical reaction between the active element (often in the form of an alkoxide) and the hydroxyl groups of the support. One of the alkoxide ligands reacts with a surface hydroxyl of the support to produce a support-active phase bond and the corresponding alcohol. During calcination of the impregnated oxide, alkenes are formed from the destruction of the surface phase. The typical reaction used to produce vanadium oxide monolayers is shown in Figure 2.2.

The grafting method usually involves wet impregnation of the support with a nonaqueous solution of the active element which is then filtered and the impregnated catalyst (filtrate) is washed. This impregnation procedure has been modified slightly for this work by employing incipient wetness impregnation of the appropriate solution.

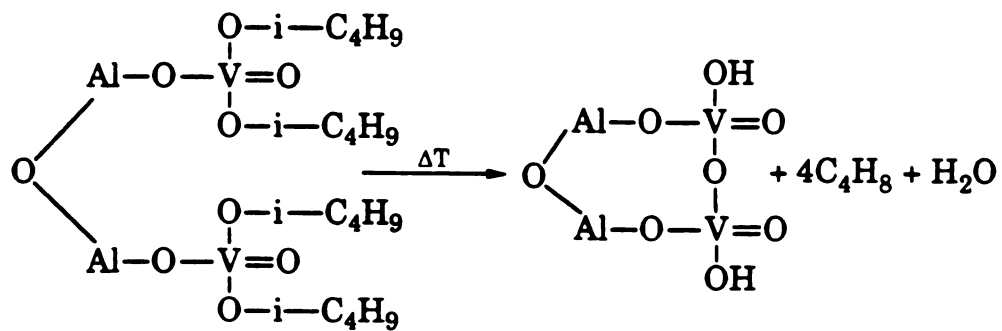
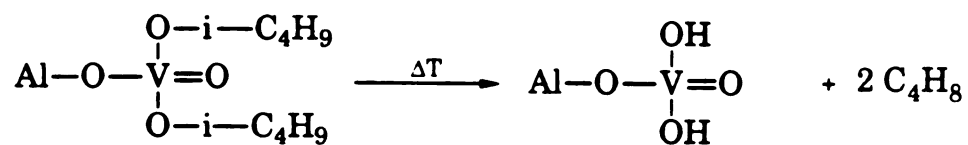
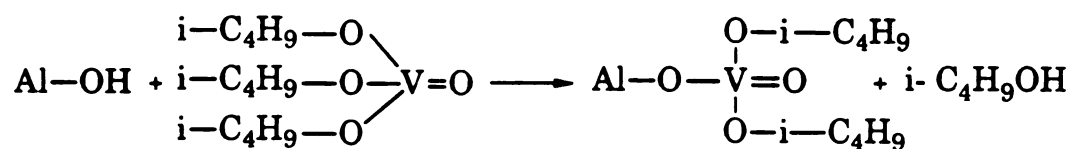


Figure 2.2. Reaction of metal alkoxide with support. (From *J. Catal.*, 101, 1, 1986).

2.2. Characterization of Heterogeneous Catalysts

2.2.1. Bulk Characterization

In order to understand the effect of preparation method, composition and pretreatment on the structure of heterogeneous catalysts, a variety of bulk characterization methods should be used. The bulk characterization methods that provide important information in this study are the Brunauer-Emmett-Teller (BET) method for measuring surface area, X-ray diffraction (XRD), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and electron paramagnetic resonance (EPR).

Surface Area. Catalyst surface areas can be determined using the Brunauer-Emmett-Teller (BET) method. In this method, the Langmuir adsorption isotherm is extended to multilayer adsorption. The first layer is as assumed in the Langmuir adsorption isotherm. For subsequent layers, the rate of adsorption is assumed to be proportional to the fraction of the lower layers which are vacant. The summation over an infinite number of adsorbed layers is defined by the following equation [11]:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)}{V_m C P_0} \quad (1)$$

where C is a constant related to the heat of adsorption and liquefaction of the gas, V_m is the monolayer capacity (cm^3 STP), V is the volume of the adsorbate at STP (cm^3/mole STP), P is the pressure of the adsorbate, and P_0 is the total pressure.

X-ray Diffraction. X-ray diffraction (XRD) can be used to identify crystalline phases with particle sizes greater than or equal to 3.0 nm. The particle size can be calculated from line broadening measurements using the Scherrer equation [12]:

$$\bar{d} = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

where $\bar{d}$ is the mean dimension of the particle, K is a constant (particle shape factor) taken as 0.9 (for cubic particles), β is the full width-half maximum of the diffraction line, λ is the X-ray wavelength, and θ is the angle between the atomic plane of both the incident and reflected beams. In addition, semi-quantitative XRD analysis can be performed in order to determine the weight percent of crystalline phases present in a catalyst series. In this procedure, a physical mixture of the phases are ground in order to produce a homogenous mixture. The areas of the peaks of interest are measured and used to generate a calibration plot. Comparison of intensity ratios measured for the catalyst and the physical mixtures can be used to determine the amount of crystalline phases present in the catalysts. This method requires the particle sizes of the active phase to be similar in the catalyst series and the physical mixture of components.

Nuclear Magnetic Resonance. Solid-state NMR is able to provide qualitative information about chemically distinct sites, clarify physical states (coordination) [13], and also provide quantitative information [14]. Since only the local environment of the atom is probed, NMR is well suited for the structural analysis of systems that do not have long range order. The type of interactions involved in solid-state NMR are direct dipole-dipole coupling between nuclei, interaction of the nuclei with electrons in the environment creating chemical shifts, and quadrupolar interactions with electric field gradients.

Infrared Spectroscopy. Infrared spectroscopy (IR) has been useful for obtaining information about the structure of catalysts and species adsorbed on the catalyst surface. IR has wide applicability in the study of dispersed metal or oxide catalysts. In addition, spectra can be readily be acquired at high temperature and pressure. Thus one may study

catalysts under realistic reaction conditions and subsequently obtain information about the nature of active sites in the catalysts.

Electron Paramagnetic Resonance. Electron paramagnetic resonance (EPR) has been extensively used to study paramagnetic species of interest in catalysis such as supported metal ions, surface defects, and adsorbed molecules and ions. The extent of information obtainable from EPR data varies from a simple confirmation that an unknown paramagnetic species is present to a detailed description of the bonding and orientation of a surface complex. Factors such as spin-spin interactions, crystal field interaction and relaxation time have a significant effect on the spectrum [15]. The high sensitivity of EPR can be useful for the study of low concentrations of active phase species.

2.2.2. X-ray Photoelectron Spectroscopy (XPS)

A variety of surface analytical methods have been used to study heterogeneous catalysts. X-ray photoelectron spectroscopy (XPS) is one of the most powerful surface sensitive techniques for the study of electronic structure of filled levels of surface atoms and adsorbates. The process occurring in XPS can be illustrated as follows [16]:

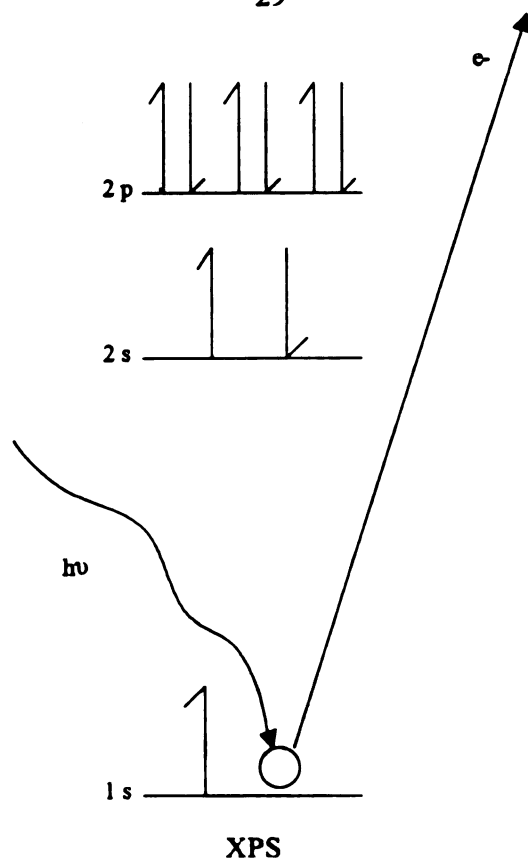


Figure 2.3. XPS process.



$$E(\text{kinetic}) = E(\text{photon}) - E(\text{binding}) \quad (4)$$

The kinetic energy of the photoemitted electron is essentially the difference between the energy of the incident photon and the binding energy of the electron. Due to a variety of processes in solids, equation 4 is more appropriately written as follows [17]:

$$E_{KE} = h\nu - E_b + E_a + E_r \quad (5)$$

where E_a is the intra-atomic relaxation energy and E_r is the extra-atomic relaxation energy associated with the solid environment. These relaxation shifts result when a core hole is created by photoionization. When this occurs, other electrons relax to lower energy states and partially screen the hole and thus make more energy available to the outgoing photoelectron.

XPS can be used to obtain qualitative and quantitative information about surface species. Even though XPS is dominated by atomic rather than solid-state effects, the local electronic environment in the solid can influence the observed peak position and line shapes through both initial and final state effects. Initial state effects refer to shifts in the original binding energy due to changes in the electronic environment of the atom. Final state effects are shifts associated with intra- and extra-atomic relaxations [17].

The signal intensity, I_i , of XPS can be related to the concentration by the following expression:

$$I_i = I_0 \eta_i D(\epsilon_i) \lambda(\epsilon_i) \quad (6)$$

where I_0 is the X-ray flux, η_i is the concentration, σ_i is the photoelectron cross section [18], $D(\epsilon_i)$ is the efficiency of the analyzer, and $\lambda(\epsilon_i)$ is the mean free path of the photoelectron.

Inelastic mean free path or escape depth (λ) of low energy electrons in the solid is a key parameter in describing the surface sensitivity of XPS. To obtain the mean free path the following expression is used [19]:

$$\lambda(\epsilon) = \frac{\epsilon}{[a(\ln \epsilon + b)]} \quad (7)$$

where $\lambda(\epsilon)$ is the mean free path of the excited electron with energy ϵ and a and b depend on the electron concentration of the solid.

In order to obtain quantitative information about catalysts, a number of models have been proposed to relate active phase/support peak intensity ratios to catalyst structure. It has been shown by Defosse et al. [20] that one can calculate the theoretical intensity ratio (I_p^0/I_s^0) expected for a supported phase (p) atomically dispersed on a carrier (s). Kerkhof and Moulijn [21] extended the Defosse model and derived expressions based on a model catalyst that consists of sheets of support with cubic particles of active phases deposited between the support layers (Figure 2.4).

For species dispersed as monolayers, the relationship is given by the following equation:

$$\left(\frac{I_p^0}{I_s^0} \right)_{\text{monolayer}} = \left(\frac{p}{s} \right)_b \frac{D(\epsilon_p) \sigma_p \beta_1 (1 + e^{-\beta_2})}{D(\epsilon_s) \sigma_s 2(1 - e^{-\beta_2})} \quad (8)$$

where I_p is the intensity of the electrons from element p in the supported phase, I_s is the intensity of the electrons from element s in the carrier, σ_p and σ_s are the photoelectron cross sections of the respective elements, $D(\epsilon)_{p,s}$ are the detector efficiencies, $\epsilon_{p,s}$ are the kinetic energies of the electrons, and $\beta_{1,2}$ is the thickness (t) per mean escape depth of the photoelectrons from the support (λ_s) or from the promoter (λ_p). For crystallites, the equation can be simplified to:

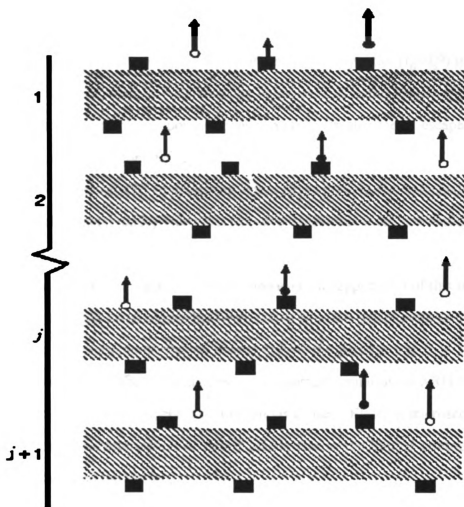


Figure 2.4. Model of the catalyst particle. (From *J. Phys. Chem.*, **83**, 1612, 1979).

$$\left(\frac{I_p}{I_s}\right)_{\text{crtl}} = \left(\frac{I_p^0}{I_s^0}\right) \left[\frac{1 - e^{\left(\frac{-d}{\lambda_p}\right)}}{\frac{d}{\lambda_p}} \right] \quad (9)$$

where $(I_p/I_s)_{\text{crtl}}$ is the experimentally determined intensity ratio, (I_p^0/I_s^0) is the theoretical monolayer intensity ratio calculated using equation 9, d is the length of the edge of the cubic crystallites of the deposited phase, and λ_p is the mean escape depth of the photoelectron in the promoter [22].

The ability of XPS to determine active phase particle size independent of chemical state (metal or metal oxide) offers distinct advantages over more conventional methods of catalyst characterization. For example, chemisorption may be used to determine the average particle size of supported metals; however, the application of this technique to the study of supported metal oxides has been limited to a few select systems. Using XRD, it is possible to determine crystalline phases only if the particle size is ≥ 3.0 nm and the phase is present in sufficient quantities. An important limitation of XRD is that it cannot be used to study highly dispersed or amorphous phases. Electron microscopy may not be useful for the characterization of mixed oxides due to the limited contrast between the support phase and the carrier.

An important capability of surface spectroscopy is the ability to observe changes in the surface structure. Surface reactions provide useful information for understanding changes in the surface structure that result during reactions (Figure 2.5). Species which strongly interact with the support tend to undergo fewer chemical and structural changes during reactive gas treatment in comparison to weakly interacting phases. By choosing reactive gases that are involved in oxidation or ammoxidation reactions, it is possible to

study the reactivity of catalyst phases under conditions similar to those in actual reaction conditions. *In situ* surface characterization of catalysts reacted with reducing molecules such as H₂, NH₃, CO and hydrocarbons will be performed using a preparation chamber attached directly to the surface science instrument (Figure 2.6).

2.2.3. Catalytic Activity

The catalytic activity experiments reported in this work were performed in a differential reactor as shown in Figure 2.7. As shown in the figure, the gases are passed through a zeolite bed to remove water. The flow of the gas is controlled by mass flow controllers. The gas mixture can either be routed to the reactor or can bypass the reactor for direct analysis of the gas stream prior to reaction. By correlating activity with the catalyst structure it will be possible to identify active sites of the catalysts.

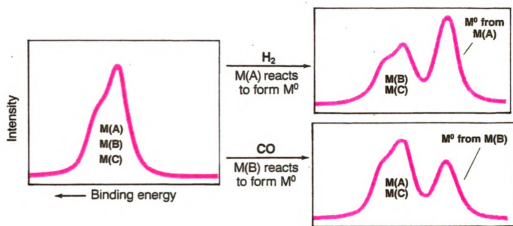


Figure 2.5. Protocol for study of heterogeneous catalysts by reactive gas treatment combined with XPS. (From *Anal. Chem.*, **58**(12), 1184 A, 1986).

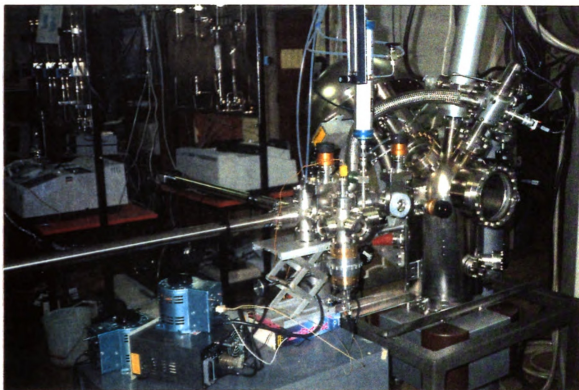


Figure 2.6. Reaction chamber.

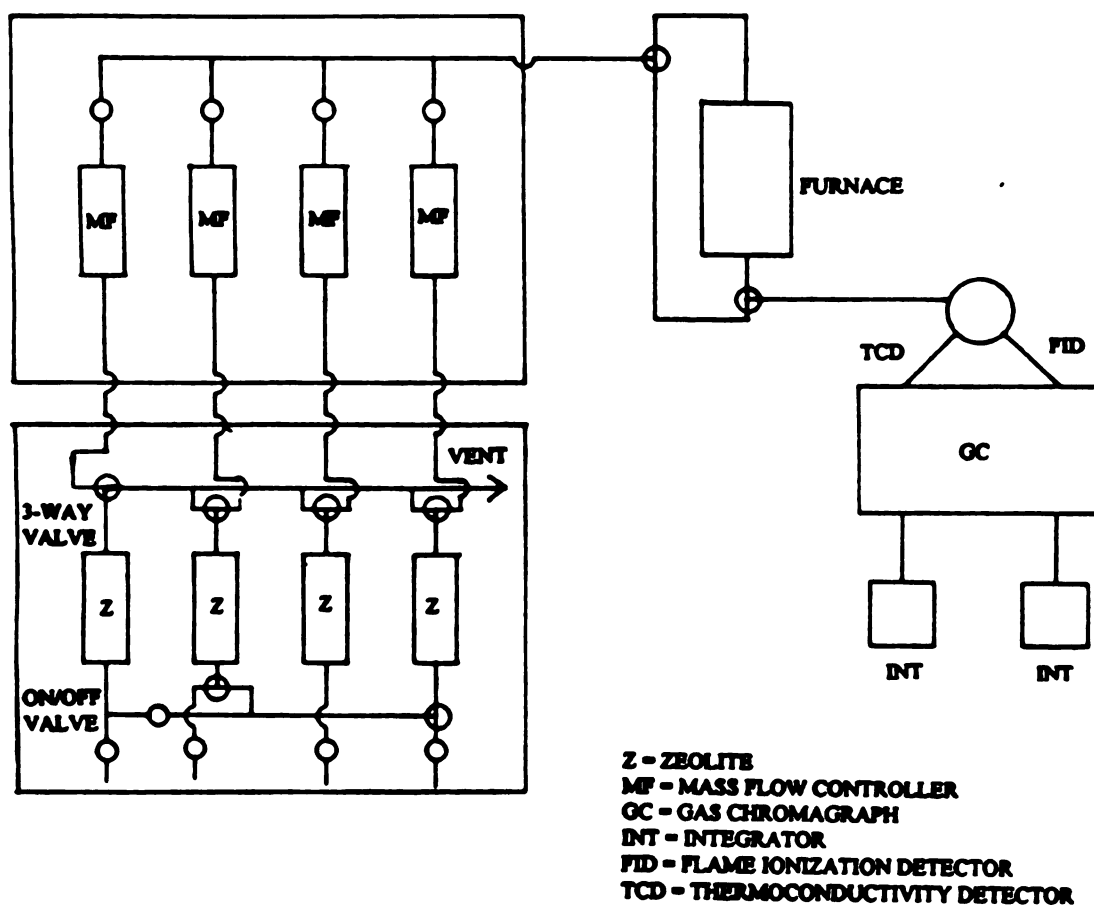


Figure 2.7. Catalytic reactor.

References

1. F. Roozeboom, D.D. Cordingley, and P.J. Gellings, *J. Catal.*, **68**, 464, 1981.
2. I.E. Wachs, R.Y. Saleh, S.S. Chan, and C.C. Chersich, *Appl. Catal.*, **15**, 339, 1985.
3. P.L. Villa, "Catalyst Deactivation," B.Delmon and G.F. Fromont ed., Elsevier, Amsterdam, p. 103, 1980.
4. J.C.W. Chien, *J. Amer. Chem. Soc.*, **93**, 4675, 1971.
5. H. Praliaud and M.V. Mathieu, *J. Chim. Phys.*, **73**, 689, 1976.
6. V.A. Khalif, E.L. Aptekar', O.V. Krylov, and G. Öhlmann, *Kinet. Catal. (USSR)*, **18**, 867, 1977.
7. F. Roozeboom, T. Fransen, P. Mars, and P.J. Gellings, *Z. Anorg. Allg. Chem.*, **25**, 449, 1979.
8. E.T.C. Vogt, A.J. van Dillen, J.W. Geus, and F.J.J.G. Janssen, *Catal. Today*, **2**, 569, 1988.
9. S. Shan and D.Hoenicke, *Chem.-Ing.-Tech.*, **61**, 321, 1989.
10. A. Baiker and A. Wokaun, *Naturwiss*, **76**, 168, 1989.
11. C.N. Satterfield, "Heterogenous Catalysis in Practice," New York, McGraw-Hill, 1980.
12. H.P. Klug and L.E. Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials," New York, Wiley-Interscience Publications, 1974.
13. C. Dybowski, *Chemetech.*, **March**, 186, 1985.
14. B.C. Gerstein, *Anal. Chem.*, **55**(7), 782A, 1983.
15. W.N. Delgass, G.L. Haller, R. Kellerman, and J.H. Lunsford, "Spectroscopy in Heterogeneous Catalysis," Academic Press, 1979.
16. D.M. Hercules and S.H. Hercules, *J. Chem. Ed.*, **61**(6), 483, 1984.
17. D.P. Woodruff and T.A. Delchar, "Modern Techniques of Surface Science," Cambridge, Cambridge University Press, 1986.
18. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 129, 1979.
19. D. R. Penn, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 29, 1976.
20. C. Defosse, P. Canesson, P. G. Rouxlet, and B. Delmon, *J. Catal.*, **51**, 269, 1979.
21. F. P. J. M. Kerkhof and J. A. Moulijn, *J. Phys. Chem.*, **83**, 1612, 1979.
22. M. Houalla, in "Preparation of Catalysts III", Elsevier, Amsterdam, 273, 1983.

Chapter 3

Vanadium Oxide/Aluminum Antimonate

3.1. Introduction

Considerable research effort has been focused on the development of selective oxidation and ammoxidation catalysts for the activation of less expensive feedstocks such as propane, propylene and methane. Several researchers have reported that vanadium antimonate catalysts are promising systems for ammoxidation of propylene [1] and propane [2] to acrylonitrile. Typical industrial catalysts are prepared by mixing a hydrosol or gel of the carrier with a slurry or solution containing the active phase(s) and the promoters, such as W and/or Mo. This procedure can produce very complicated catalyst structures that make comprehensive characterization difficult. Thus, the effect of surface structure on the properties of the catalyst and active site(s) are not well known. In order to understand the influence of the catalyst structure on alkane or alkene activation, a simple catalytic system must be examined.

Centi et al. [3] have investigated the structure and selective oxidation and ammoxidation of propane activity for VSbO_x mixed oxides supported on SiO₂, Al₂O₃, and TiO₂ and promoted with W or Mo. Their work suggests that VSbO_x phase plus Sb₂O₅ is not the active phase for ammoxidation. Instead, they proposed that AlSbO₄ rutile phase modified with V is the active phase for the formation of propylene and V or other redox elements having M=O bonds (W or Mo) are needed to form acrolein or acrylonitrile. Although VSbO_x/Al₂O₃ is not as complex as the commercial catalysts, further understanding of propane and propylene activation would be obtained by studying the interaction of the pure phases believed to be responsible for selective oxidation and ammoxidation.

Recently, Volta et al. [4,5] have examined the structure and propane oxidation activity of vanadium oxide on AlNbO_4 . AlNbO_4 was chosen because of the structural similarity between AlNbO_4 and TiO_2 . These researchers showed that it is possible to control the structure and reactivity of vanadia monolayers by modifying the local structure of the oxide support. They also found that the AlNbO_4 disorganized structure is present and has good selectivity for the oxidative dehydrogenation of propane into propylene.

This work will correlate surface structure with propylene oxidation activity for V oxide catalysts supported on AlSbO_4 . The focus will be on defining the nature of the V- AlSbO_4 interaction and influence of V dispersion and reactivity on the catalytic properties of the mixed oxides. In order to determine structure and reactivity of the species in the mixed oxide catalysts, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), solid-state nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR) will be used. Structural information will be correlated with propylene oxidation activity measurements in order to establish the nature of propylene activation site(s) in V/ AlSbO_4 mixed oxide catalysts.

3.2. Experimental

Catalyst Preparation. AlSbO_4 was prepared by coprecipitation of a 1:1 atomic ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (J.T. Baker, A.C.S. grade) dissolved in deionized water and SbCl_5 (Aldrich, 99%). SbCl_5 was added to a vigorously stirred solution of $\text{Al}(\text{NO}_3)_3$ over a 30 minute period. NH_4OH (J.T. Baker, A.C.S. grade) was added until the solution pH reached 6-7. The neutralized solution was allowed to stir for 1 hour. The precipitate formed was filtered and washed with deionized water, dried in air at 120°C for 12 hours, ground to produce a homogeneous mixture, and calcined in air at 750°C for 12 hours. The resulting AlSbO_4 support had a pore volume of 0.1 ml/g and a surface area of 155 m^2/g . Prior to impregnation, the support was calcined at 500°C for 12 hours.

V/AlSbO₄ catalysts were prepared by pore volume impregnation of AlSbO₄ using vanadium triisopropoxide oxide (Alfa, 95-99%). The catalysts were dried under nitrogen for 48 hours at 25°C, dried in air for 12 hours at 120°C and calcined in air at 500°C for 12 hours. The vanadium content varied from 0 to 25 wt % V₂O₅ (V/Al atomic ratio of 0 to 0.78). Catalysts will be designated V# where # is the weight percent vanadium as V₂O₅.

Standard Materials. VO₂ (99.9%) and V₂O₃ (99%) were obtained from Aldrich. V₂O₅ was prepared by calcining NH₄VO₃ (Johnson Matthey, 99.99%) in air at 450°C for 4 hours. Sb₂O₅ was prepared by the addition of SbCl₅ to deionized water under vigorous stirring. The pH of the solution was adjusted to 6-7. The precipitate formed was filtered and washed with deionized water, dried in air at 120°C for 12 hours and calcined at 500°C for 12 hours. XRD patterns of all standard compounds matched the appropriate ASTM powder diffraction file.

BET Surface Area. Surface area measurements were determined using a QuantaChrome Quantasorb Jr. Sorption System. Approximately 0.10 grams of the catalyst was outgased between 165°-170°C for 12 hours prior to absorption measurements. Measurements were made using relative pressures of N₂ to He of 0.05, 0.08, and 0.15 (surface area of N₂ = 0.162 nm²) at 77 K. Data were processed using a Macintosh computer.

X-ray Diffraction. X-ray powder diffraction patterns were obtained using a Rigaku XRD diffractometer which employs Cu K α radiation (1.541838 Å). The x-ray was operated at 45 kilovolts and 100 milliamps. The patterns were scanned between 10°-75° (2 theta) at a scan rate of 0.1 °/min. with DS and SS = 0.5. Powdered samples were mounted on glass slides by pressing the powder in an indentation on one side of the slide. Particle sizes were determined from line broadening measurements using the Scherrer equation [6]:

$$\bar{d} = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where $\bar{d}$ is the mean dimension of the particle, K is a constant (particle shape factor) taken as 0.9 (for cubic particles), β is the full width-half maximum of the V_2O_5 $\langle 001 \rangle$ diffraction line, λ is the X-ray wavelength, and θ is the angle between the atomic plane of both the incident and reflected beams. Semi-quantitative XRD has been performed using physical mixtures of V_2O_5 and $AlSbO_4$ (0.2 wt %, 0.5 wt %, and 1.0 wt % V_2O_5). The areas of the V_2O_5 $\langle 001 \rangle$ and $AlSbO_4$ $\langle 110 \rangle$ peaks were measured and used to generate a calibration curve that can be used to determine the amount of crystalline V_2O_5 present in the $V/AlSbO_4$ catalysts. Peak areas were obtained using Googly software [7] and a linear background was assumed over the peak base.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) data were obtained using a Perkin-Elmer spectrometer that is equipped with a Mg (1253.6 eV)/Al (1486.6 eV) dual anode and a 10-360 hemispherical analyzer with an omnifocus small spot lens. Samples were mounted as powders on double-sided sticky tape or spray coated on glass slides. Spray coated samples were prepared by air brushing a 10% suspension of the catalyst (20% deionized water and 80% acetone) onto a glass slide heated at 60°C. XPS binding energies of the catalyst were referenced to the Al 2p (74.5 eV) peak. The binding energies for standard compounds were referenced to the C 1s (284.6 eV). Peak areas and binding energies were obtained using Googly software. XPS binding energies were measured with a precision of ± 0.2 eV, or better.

In situ XPS analyses of spray coated $V/AlSbO_4$ were performed using a reactor attached directly to the spectrometer. The samples were initially analyzed, then reacted first with 100 cc/min mixture of 8.0% O_2 (99.98%) and 92% He (99.9%) for 1 hour at

350°C and then with 100 cc/min 1.7% propylene (99.9%), 8.0% O₂ and 90.3% He for 10 minutes at 200°C.

Quantitative XPS. A number of models have been proposed to relate active phase/support XPS peak intensity ratios to catalyst structure. It has been shown by Defosse et al. [8] that one can calculate the theoretical intensity ratio (I_p^0/I_s^0) expected for a supported phase (p) atomically dispersed on a carrier (s). Kerkhof and Moulijn [9] extended the Defosse model and derived expressions based on model catalysts that consist of sheets of support with cubic particles of active phase deposited between the support layers. The photoelectron cross-sections (σ) and mean escape depths (λ) of the photoelectrons used in the calculations are taken from Scofield [10] and Penn [11], respectively. For species dispersed as monolayers, the relationship is given by the following equation:

$$\left(\frac{I_p^0}{I_s^0} \right)_{\text{monolayer}} = \left(\frac{p}{s} \right)_b \frac{D(e_p)\sigma_p\beta_1(1+e^{-\beta_2})}{D(e_s)\sigma_s 2(1-e^{-\beta_2})} \quad (2)$$

where I_p^0 is the intensity of the electrons from element p in the supported phase, I_s^0 is the intensity of electrons from element s in the carrier, σ_p and σ_s are photoelectron cross sections of the respective elements, $D(e_{p,s})$ are detector efficiencies, $e_{p,s}$ are the kinetic energies of the electrons, and $\beta_{1,2}$ is the thickness (t) per the mean escape depth of the photoelectron from the support (λ_s) or the promoter (λ_p). This model predicts a linear increase in the intensity ratio of the supported phase (p) to the carrier (s) as the (p/s) atomic ratio is increased.

Infrared Spectroscopy. Infrared spectra were obtained using a Mattson 3020 FTIR spectrometer with a DTGS detector. The catalyst was suspended in a 80% acetone

20% water mixture and sprayed on a 13x2 mm KBr disk heated at 60°C. Spectra were obtained with 2 cm⁻¹ resolution and both background and sample had 32 scans performed. Data acquisition were performed using a FIRST software package. Data manipulation were performed using Googly software. A linear background was subtracted to produce Figure 3.6.

Nuclear Magnetic Resonance. Solid-state nuclear magnetic resonance experiments were performed using a Varian VXR 400 spectrometer. The powdered catalysts were packed into a zirconium oxide roater. The samples were spun in a Bruker MAS probe at 4 kHz. The frequency used for aluminum catalysts was 104.230 MHz.

Wide-line solid-state NMR experiments were also performed. The amplifier is from American Microwave Technology and the probe is a standard Varian wide-line probe. The powder samples were placed in a quartz tube and then placed in the wide-line probe. The frequency used for the vanadium catalysts was 105.152 MHz. A SUN workstation was used to operate the spectrometer and process the data.

Electron Paramagnetic Resonance. Electron paramagnetic resonance data for V/AlSbO₄ catalysts were obtained using Bruker ER 300D spectrometer. A Hewlett Packard 5245L electronic counter with a 5255A frequency converter plug in and a Bruker ERO35M gaussmeter were used to measure microwave frequency and magnetic field, respectively. The cavity used was a rectangular TE₁₀₂. The samples were run as powders after reaction in 1.7% propylene, 8.0% O₂ and 90.3% He.

Propylene Oxidation Activity Measurements. Catalytic activity experiments were carried out in a differential type flow reactor at low conversion (<10%) with O₂/propylene/He (8.0/1.7/90.3%) at a temperature of 250°C. The catalysts were pretreated at 350°C for 3 hours with a 8.0% O₂/92% He mixture. For both pretreatment and reactions, the flow rate was 100 cc/minute. Approximately 0.2 grams were used for each reaction. Reactions reached steady-state after 11 hours. The gas flow rates were held constant with Brooks 5850 and Porter 201 mass flow controllers. The reactor

temperature was controlled with an Omega CN 1200 controller. Product gases were analyzed with a Varian 3700 gas chromatograph equipped with a TCD (for CO, CO₂) and FID (for hydrocarbon, acrolein, and acetaldehyde). The column used for permanent gas separation was a 5 ft. 60/80 mesh Carboxen (Supelco) column. For hydrocarbon and acrolein separation a 5 ft 80/100 Porapak QS column was used. The chromatograph was interfaced to a Hewlett-Packard 3394A integrator. The column temperature was programmed from 55°C to 190°C with analysis time of 30 minutes to allow complete separation of all components. Selectivities are reported for catalysts operated at similar conversion.

3.3. Results

AlSbO₄. The BET surface area of the AlSbO₄ support is given in Table 3.1. The XRD powder pattern of the support (Figure 3.1) matches results reported in the literature [12]. The AlSbO₄ particle size determined using x-ray diffraction line broadening calculations (equation 1) is 2.7 nm. No other peaks due to antimony oxides or aluminum oxides were observed. ²⁷Al MAS solid-state NMR of the aluminum antimonate support has been performed and peaks at 1, 34, and -31 ppm in the NMR spectrum were observed (Figure 3.2). The FTIR spectrum of the support was also obtained and no peaks were observed between approximately 920 cm⁻¹ and 1050 cm⁻¹ (the region of interest of the vanadium oxide). The XPS Sb 3d_{3/2} binding energy measured for the support was found to be 540.5 eV. The XPS binding energy for Sb₂O₅ was 540.5 eV. The XPS Sb3d_{3/2}/Al 2p intensity ratio indicates that Sb/Al atomic ratio in the surface of the AlSbO₄ support is 1.0.

Vanadium/Aluminum Antimonate. Variation in the BET surface area of the V/AlSbO₄ catalysts as a function of vanadium content is shown in Table 3.1. The surface area decreases from 140 to 108 m²/g as the V/Al atomic ratio increases from 0.12 to 0.78

Table 3.1. BET surface area (m²/g) of V₂O₅/AlSbO₄ catalysts.

Atomic Ratio V/Al	Weight % V ₂ O ₅	Surface Area (m ² /g)
0	0	155
0.12	5	140
0.26	10	132
0.41	15	123
0.58	20	111
0.78	25	108

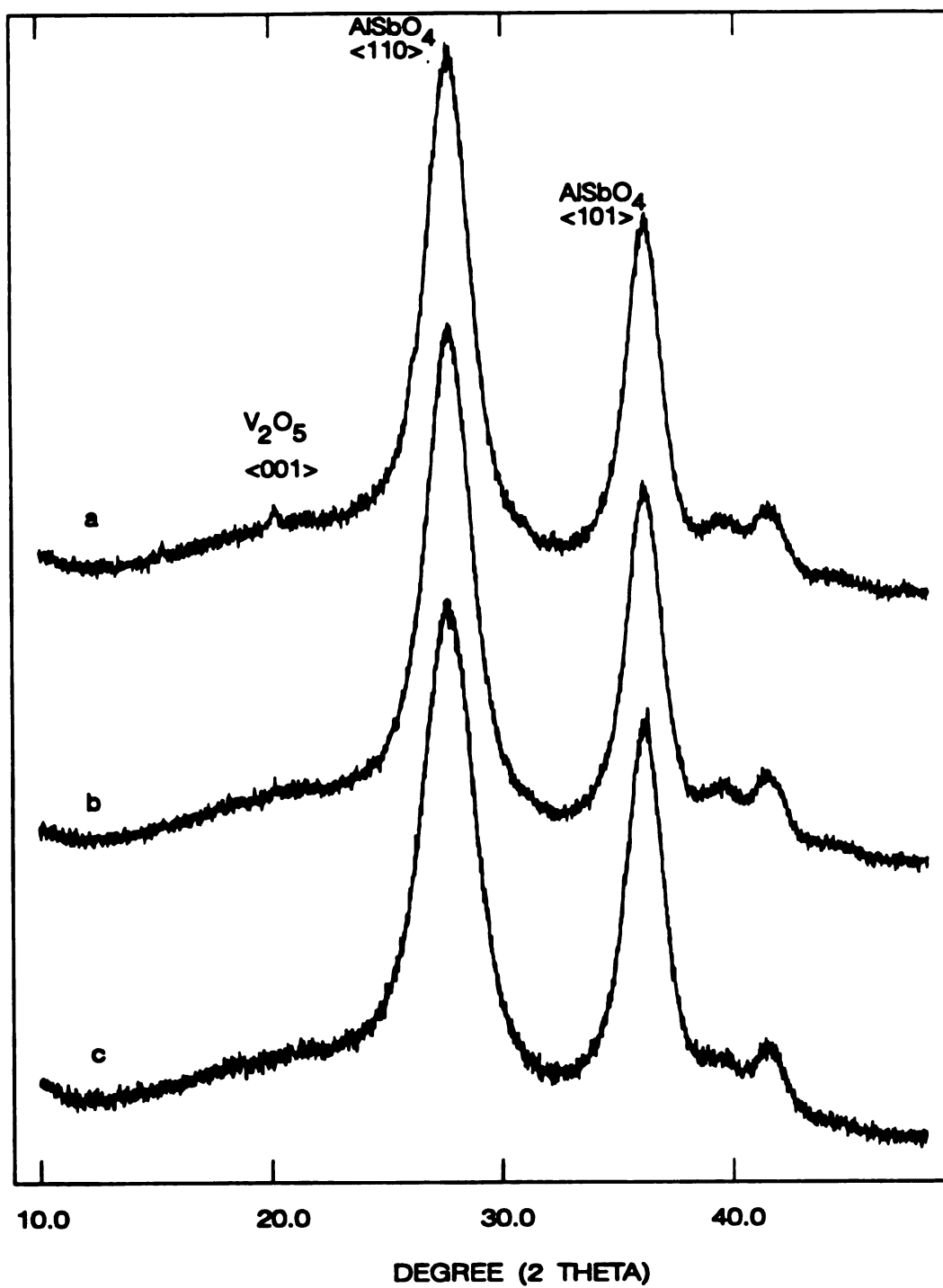


Figure 3.1. XRD of $V_2O_5/AlSbO_4$ a) V25, b) V20, and c) V0 catalysts.

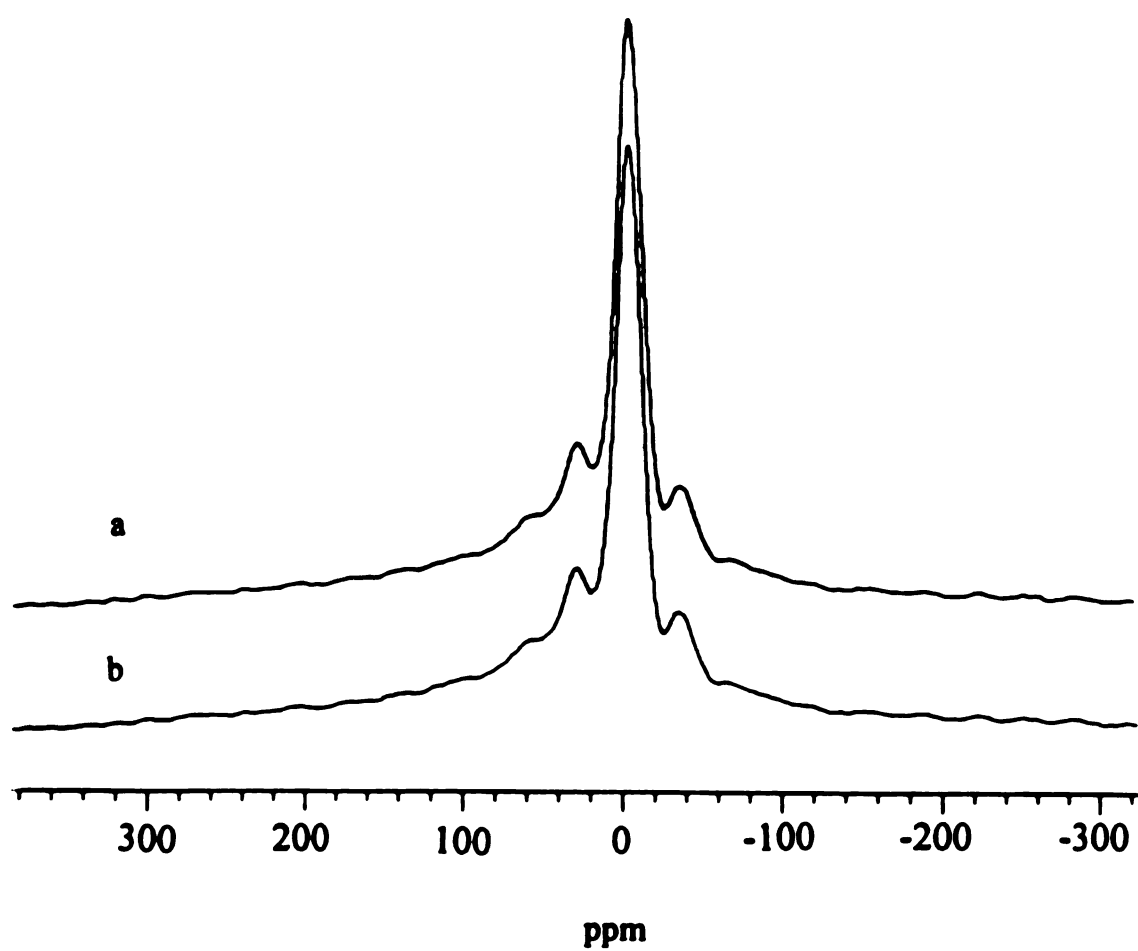


Figure 3.2. ^{27}Al MAS NMR of a) V25 and b) V0 catalysts.

(5 wt.% to 25 wt.% V_2O_5). However, corrections made for active phase loading indicate that the surface area of the support does not change.

For $V/AlSbO_4$ catalysts with V/Al atomic ratios of < 0.78 , XRD patterns showed peaks characteristic only of the $AlSbO_4$ carrier (Figure 3.1). The diffraction pattern measured for the V25 catalysts showed peaks characteristic of $AlSbO_4$ and crystalline V_2O_5 . For the V25 catalyst, XRD line broadening calculations (equation 1) indicated that the particle size of the V_2O_5 crystallites was 29 nm (Table 3.2). Figure 3.3 shows the variation of the V_2O_5 $<001>/AlSbO_4$ $<110>$ intensity ratios measured for 0.2, 0.5 and 1.0 wt.% $V_2O_5/AlSbO_4$ physical mixtures. The value measured for the V25 catalyst with is also given. The results indicate that the amount of V_2O_5 crystallite in the catalyst is less than 0.1 wt.% V_2O_5 .

XPS V $2p_{3/2}$ binding energies measured for the catalysts, run as powders, were found to be 517.5 ± 0.2 eV. The XPS V $2p_{3/2}$ binding energy measured for pure V_2O_5 , VO_2 and V_2O_3 were 517.5 eV, 517.3 eV and 516.5 eV, respectively. The binding energies of the Sb $3d_{3/2}$ for the series of catalysts were found to be 540.4 ± 0.2 eV. The binding energies for both vanadium and antimony are independent of vanadium loading.

XPS V $2p_{3/2}$ binding energies measured for the spray coated and propylene/ O_2 /He reacted catalysts were 517.3 ± 0.2 eV. For O_2 /He reacted catalysts the V $2p_{3/2}$ binding energies were 517.0 ± 0.3 eV. The Sb $3d_{3/2}$ for all the samples under each condition was 540.3 ± 0.2 eV. Variation in the position of the vanadium peak as a function of reaction condition measured for the V25 catalyst is shown in Figure 3.4.

Figure 3.5 shows the variation in the V $2p_{3/2}/Al$ 2p XPS intensity ratio measured for powder, spray coated, oxidized, and reacted catalysts as a function of V/Al atomic ratio. There is a linear increase in intensity ratios for the spray coated and reacted samples up to a V/Al atomic ratio of 0.58. Between an V/Al atomic ratio of 0.58 and 0.78, there is a sharp decrease in the V/Al intensity ratio measured for the spray coated and reacted samples. For the powdered samples, there is a linear increase in the V/Al intensity ratio as

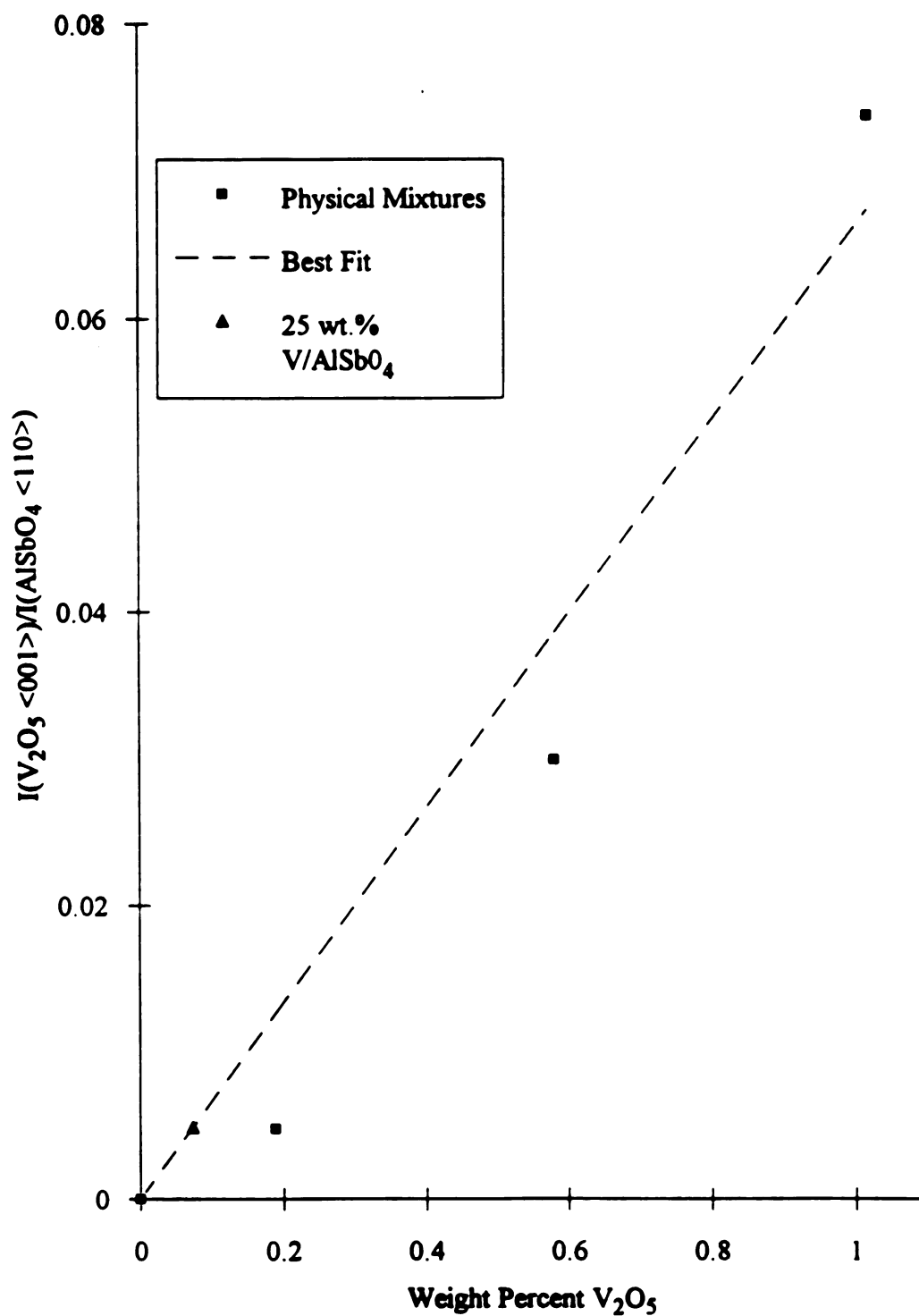


Figure 3.3. Semi-quantitative XRD for physical mixtures of V₂O₅ and AlSbO₄.

Table 3.2. Particle size for $V_2O_5/AlSbO_4$ calculated from XRD data.

V/Al Atomic Ratio	XRD Particle size (nm)
	XRD(nm)
0.12	—*
0.26	—*
0.41	—*
0.58	—*
0.78	29

* - No V_2O_5 peaks observed. Thus, no V_2O_5 particle size can be calculated.

as the V/Al atomic ratio increases. For catalysts with V/Al atomic ratios < 0.58 and V25 catalyst the intensity ratios for the powder, spray coated, and reacted samples are similar, within experimental error. The V20 V/Al intensity ratios measured for spray coated and reacted catalysts were identical, within experimental error. However, the V/Al intensity ratio measured for the powder catalyst was significantly lower than those obtained for the spray coated and reacted catalysts.

IR. Figure 3.6 shows the IR spectra measured between approximately 920 cm^{-1} and 1050 cm^{-1} for the catalysts. The spectrum measured for the V_2O_5 is shown for comparison. The spectra contains a broad band centered at 985 cm^{-1} for all loadings. As the V/Al atomic ratio increases from 0.26 to 0.41, another band appears at 995 cm^{-1} . A band at 1022 cm^{-1} (which is due to crystalline V_2O_5 [13]) is observed in the spectrum measured for the V25 catalyst.

NMR. The ^{27}Al MAS NMR spectra measured for the aluminum antimonate support and the vanadium catalyst series show one main peak at approximately 1.0 ppm and additional peaks at 34 ppm and -31 ppm (Figure 3.2). Figure 3.7 shows the wide-line solid-state NMR spectra obtained for the V5 and V25 catalysts measured at a frequency of 105.152 MHz. The vanadium peak was found to shift by 40 ppm from the 5 wt.% to the 25 wt.% catalysts.

EPR. EPR spectra were measured for the catalysts calcined at 500°C and after exposure to reaction conditions. The calcined catalyst showed no signal in the EPR spectrum. However after reaction, the catalyst showed a very broad signal due to V^{4+} with a g value of 1.98 (Figure 3.8). Hyperfine structure was observed in the spectrum measured for the V5 catalyst. However because of the concentration of the vanadium, detailed information could not be obtained. Dilution of the catalysts with support did not improve the spectra obtained.

Propylene Oxidation. Table 3.3 shows the average percent conversion and selectivity to acrolein, acetaldehyde, CO, and CO_2 measured for the V/AlSbO_4 catalysts.

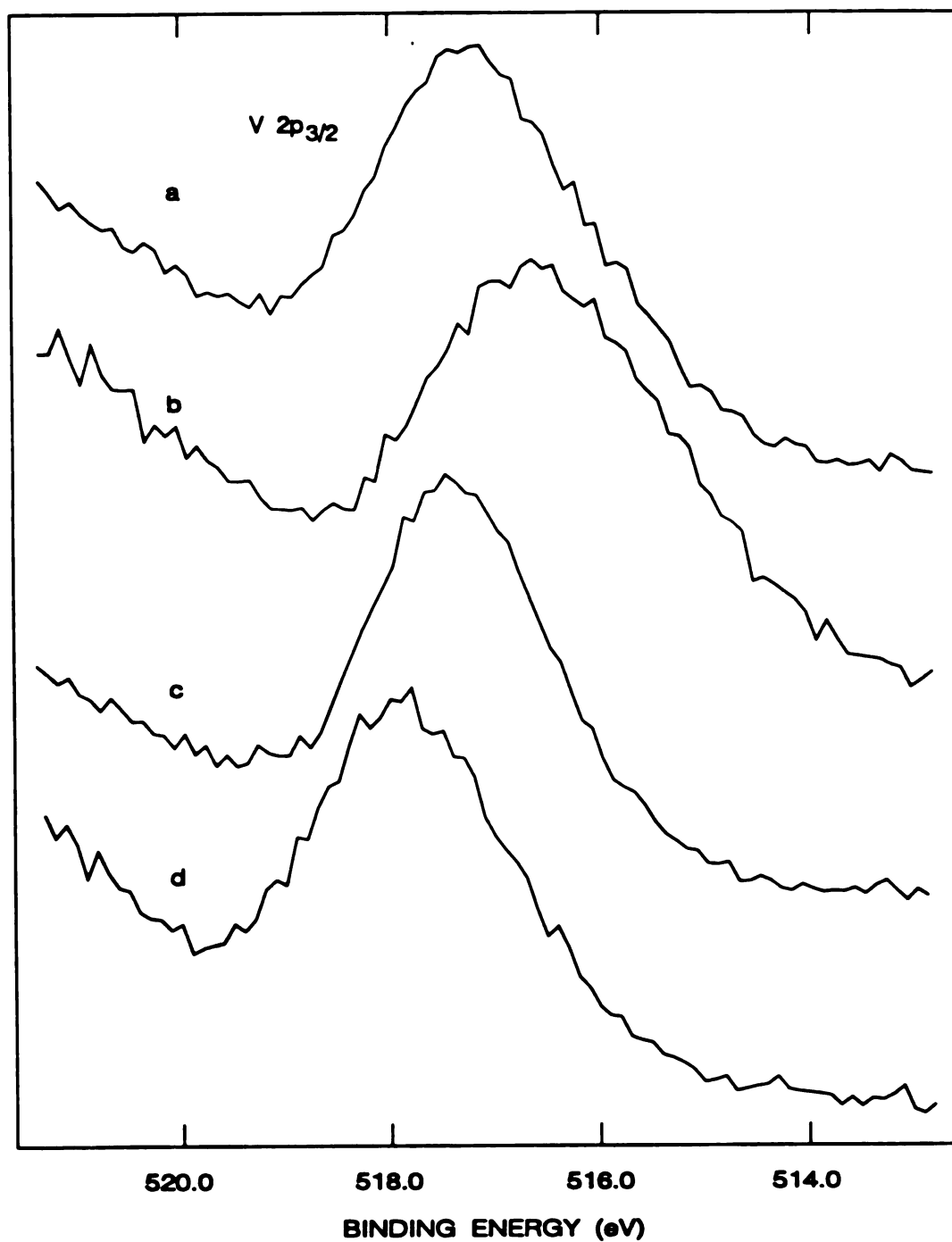


Figure 3.4. XPS spectra of V25 catalyst a) in propylene/O₂/He, b) O₂/He, c) spray coated, and d) powder.

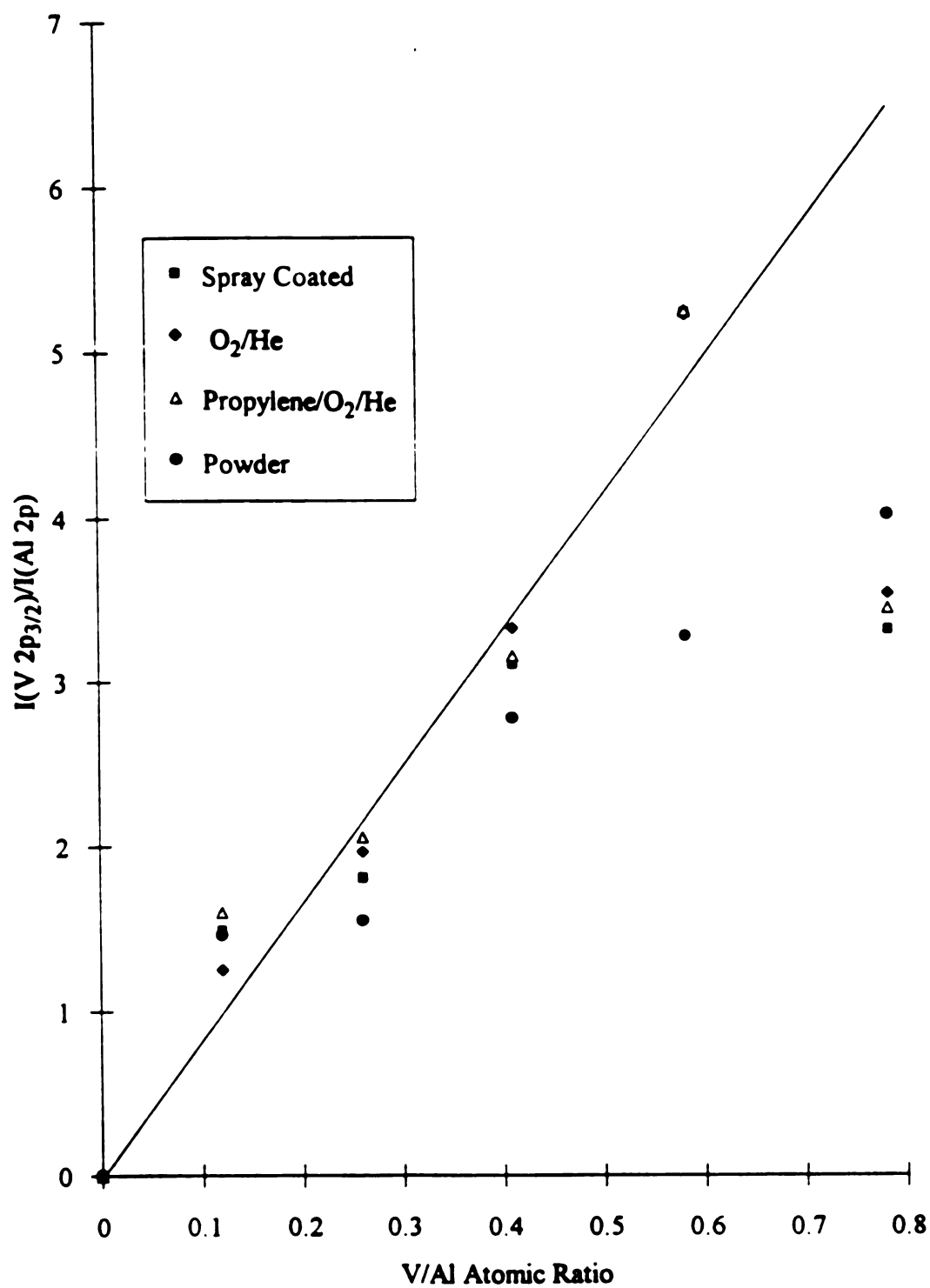


Figure 3.5. XPS intensity ratio of V 2p_{3/2}/Al 2p as a function of V/Al atomic ratio.

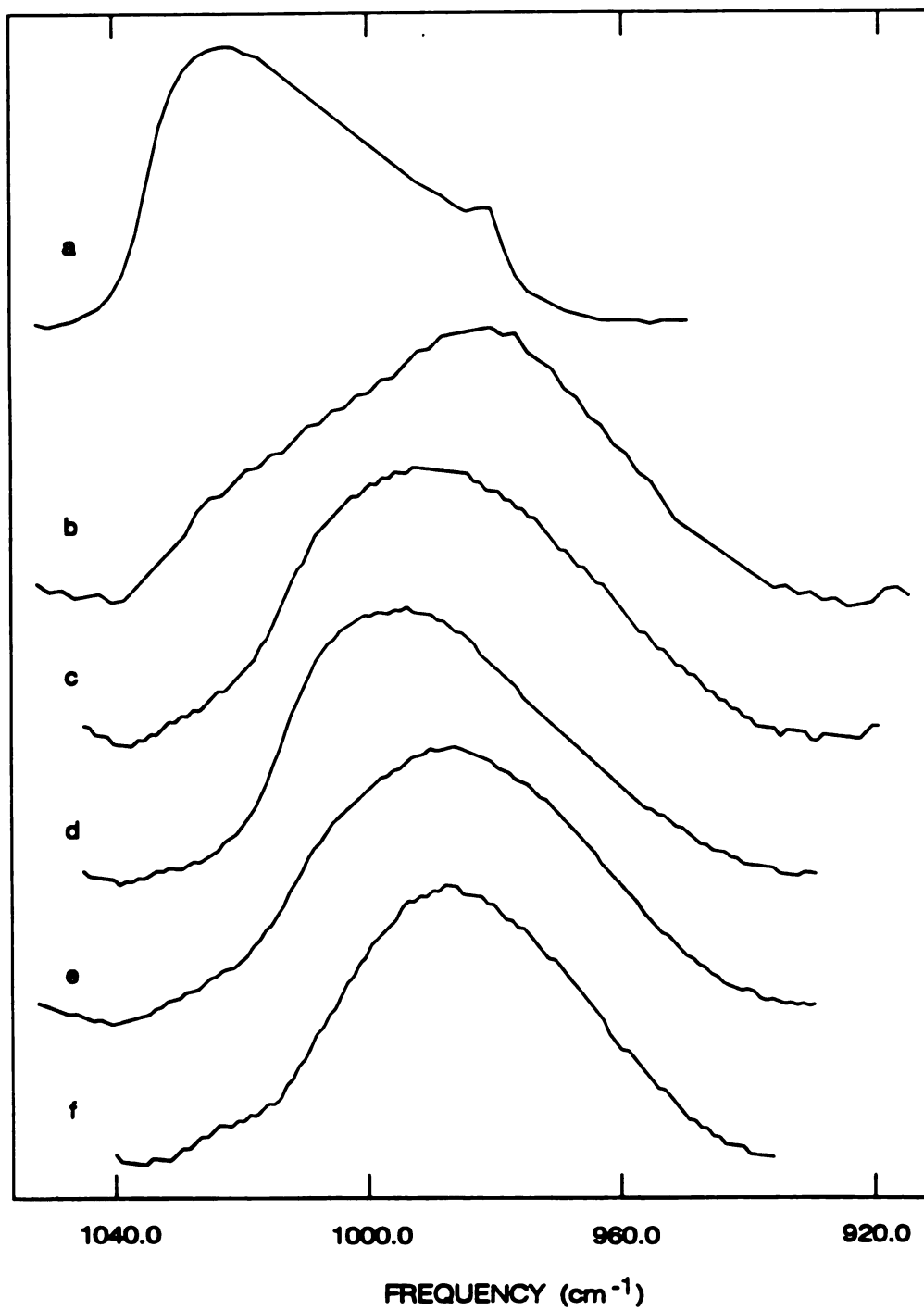


Figure 3.6. IR data of a) V_2O_5 , b) V25, c) V20, d) V15, e) V10, and f) V5 catalysts.

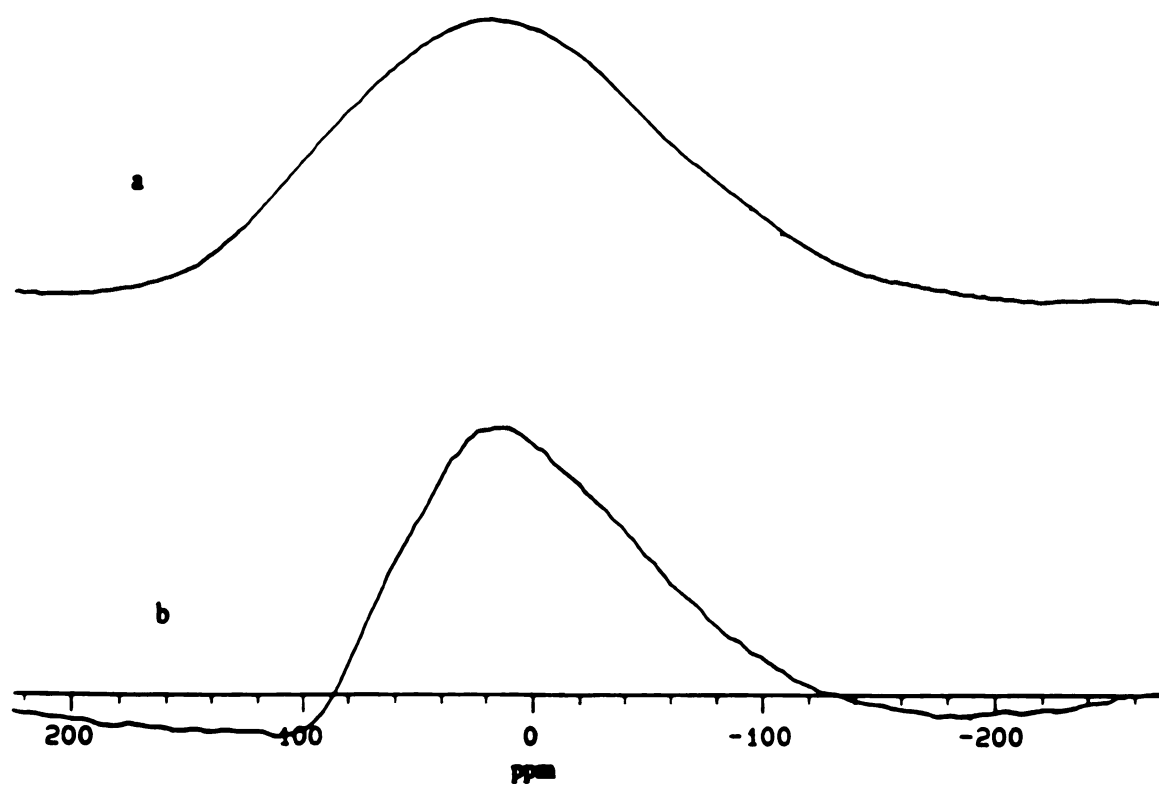


Figure 3.7. Vanadium Wide-line NMR of a) V25 and b) V5 catalysts.

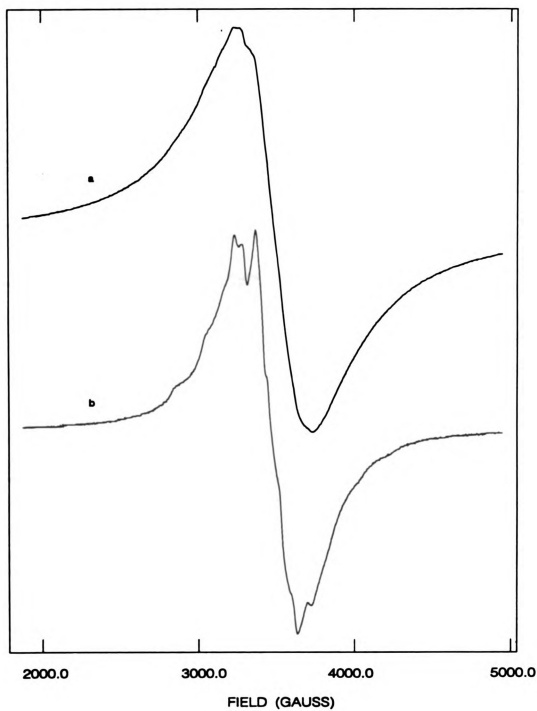


Figure 3.8. EPR V^{4+} spectra measured for reacted a) V25 and b) V5 catalysts. Spectra were collected at room temperature.

Table 3.3 Conversion and selectivity of $V_2O_5/AlSbO_4$ for propylene oxidation at 200°C and 100 cc/minute flow rate.

V/Al Atomic Ratio	Percent Conversion	Selectivity to Acetaldehyde ^a	Selectivity to Acrolein ^b	CO	CO ₂
0	0.5	37.1	59.5	3.0	<1.0
0.12	1.4	9.6	90.4	<0.1	0.1
0.26	2.2	13.6	86.2	<0.1	<0.1
0.41	3.3	17.3	82.3	<0.2	0.1
0.58	3.3	19.0	80.5	<0.2	<0.1
0.78	4.1	21.3	78.0	<0.5	<0.1
0.12	3.1	7.0	89.6	2.1	1.3
0.78	3.6	21.4	78.1	<0.4	<0.1

^a - Error bars of $\pm 20\%$.

^b - Error bars of $\pm 10\%$.

The production of carbon oxides was the highest for the pure AlSbO_4 . As the amount of vanadium oxide increases, the percent conversion increases. The addition of 5 wt.% (V5 catalyst) vanadium oxide increases the selectivity to acrolein and decreases the amount of carbon oxides formed. For higher vanadium oxide loadings, the selectivity to acrolein decreases. When the conversion of the extremes of the catalysts were similar, the selectivity to acrolein for the V5 catalyst was 89.6% and for the V25 catalyst was 78.0%. The amount of CO produced by the V5 catalyst increased from < 0.2% to 2.1% as the conversion increased.

3.4. Discussion

Aluminum Antimonate. BET, XRD, and NMR results indicate that base hydrolysis of aluminum nitrate and antimony pentachloride followed by calcination in air at 750°C results in a pure, high surface area (155 m^2/g) AlSbO_4 support. The XPS Sb 3d_{3/2} binding energy measured for AlSbO_4 carrier is consistent with the formation of Sb^{5+} expected for this compound. In addition, the Sb/Al atomic ratio determined from XPS intensity ratios (1.0) suggests that no residual aluminum or antimony phases exist in the surface of the carrier. Volta et al. [4,5] have reported that coprecipitation followed by calcination at 750°C leads to the formation of crystalline AlNbO_4 .

Structure of Calcined Vanadium/Aluminum Antimonate Catalysts. For V/ AlSbO_4 catalysts with V/Al atomic ratio ≤ 0.58 , the absence of vanadium oxide peaks in the XRD pattern indicates that no crystalline vanadium oxide phases are formed in these catalysts. However, semi-quantitative XRD analysis suggests that the V25 catalyst contains small amounts of crystalline V_2O_5 (< 0.1 wt.% V_2O_5).

The XPS V 2p_{3/2} binding energies measured for the powder and spray coated V/ AlSbO_4 catalysts indicate that the vanadium is in the +5 oxidation state for all active

phase loadings. XPS Sb 3d_{3/2} binding energy data indicates that the antimony is in the +5 oxidation state for all vanadium loadings.

The IR spectra measured for the catalysts suggest that monomeric forms of vanadium oxide are present in the catalysts because of the presence of a band centered at 985 cm⁻¹ [13]. Polymeric forms of vanadium oxide are observed in catalyst with an V/Al atomic ratio ≥ 0.26 due to the presence of the band centered at 995 cm⁻¹ [13]. For the V25, the observation of a peak at 1020 cm⁻¹ (due to V₂O₅) [13] is consistent with XRD results that show the presence of V₂O₅ crystallites.

Wide-line solid state NMR was used to determine the coordination of the vanadium in the catalysts. Eckert and Wachs [14] used wide-line NMR to study the local environments in two-dimensional vanadium(V) oxide surface layers on titania and alumina supports. Two main surface vanadium oxide species were detected with different bonding environments assigned to 4- and 6- coordinate V-O environments. Their results indicate that a marked dependence of the surface vanadium oxide structure on the metal oxide support material. For the V5 catalyst the vanadium is in a 4-coordinate environment. As the vanadium loading is increased to 25 wt.% (V25), the vanadium becomes 6-coordinate. This shift is as expected due to the change in the form of vanadium oxide from monomeric at low loadings to polymeric forms at high loadings as observed from IR data.

MAS solid-state NMR on the V/AlSbO₄ catalysts were identical to the spectrum measured for the support. The signal between 0-2 ppm is assigned to aluminum in the octahedral environment [15]. The peak at 34 ppm and -31 ppm has been attributed to pentacoordinated atoms or to aluminum in a tetrahedrally distorted coordination [16]. ²⁷Al MAS NMR spectra measured for both the support and catalysts show that there is no transformation of structure of the antimonate after the vanadium is added and the sample is calcined. Similar results were obtained by Volta et al. [17] for VO_x on AlNbO₄.

The method of preparation used was designed to produce a single monolayer of VO_x species on the AlSbO₄ surface. In order to determine the theoretical monolayer

coverage, Roozeboom et al. [18] have defined $\phi_{2.5}$ as the average area of supported surface which $\text{VO}_{2.5}$ unit occupies. For V_2O_5 , this value is approximately 0.105 nm^2 . Thus, the monolayer capacity of the AlSbO_4 support is calculated to be 22.5 wt.% V_2O_5 . From the XRD pattern we see that crystallite formation is observed between 0.58 and 0.78 atomic ratio of V_2O_5 . This is as expected based on the estimated monolayer capacity.

For V/AlSbO_4 catalysts with V/Al atomic ratio ≤ 0.58 , XPS and XRD data indicate that the vanadium is highly dispersed. XRD results show that large particles of V_2O_5 ($\sim 29 \text{ nm}$) are formed on catalysts with higher vanadium loadings. Figure 3.5 shows that the $\text{V } 2p_{3/2}/\text{Al } 2p$ intensity ratio increases linearly with vanadium loading up to a V/Al atomic ratio of 0.58. Between V/Al atomic ratio of 0.58 and 0.78 the intensity ratio decreases (observed for the spray coated and reacted samples). This suggests that the dispersion of the vanadium oxide decreases drastically at this level. In addition, this is the same loading for the formation of crystallites as observed in the XRD data and that estimated from the monolayer capacity calculation. However, the powder sample of V/Al of 0.58 does not follow the trend as seen for the spray coated and reacted samples. At present we can not determine the cause of the difference in V/Al intensity ratios measured for the spray coated, reacted, and powder V20 catalysts. Samples with $\text{V/Al} \geq 0.58$ were prepared twice and the same trend was observed.

IR results also suggest that the vanadium is highly dispersed due to the presence of bands characteristic of monomeric and polymeric vanadium oxide species. The band centered at 985 cm^{-1} is assigned to vanadate dispersed on the support as a monolayer. Distortion of the structure causes a shift of the V=O stretching band from 1020 to 985 cm^{-1} [13]. The band centered at 995 cm^{-1} is attributed to polymeric forms of vanadium on the support. The band at 1022 cm^{-1} is due to crystallite forms of V_2O_5 . The absence of a band characteristic of vanadate (950 cm^{-1}) suggests that no aluminum or antimony vanadates are present [17]. MAS NMR obtained for the support and the catalysts supports this finding. Nakagawa et al. [13] studied monolayer species of $\text{V}_2\text{O}_5/\text{TiO}_2$ and

found a shift from 1020 (crystallite V_2O_5) to 980 cm^{-1} for the $\text{V}=\text{O}$ stretching frequency. Their results lead to the conclusion that at low coverage VO_x is amorphous and at high coverage both amorphous and crystalline V_2O_5 are observed. Similar results were obtained for V_2O_5 supported on TiO_2 , Al_2O_3 , ZrO_2 , and SiO_2 deposited either from aqueous metavanadate or gaseous VOCl_3 precursors [19-21].

Bond et al. [22] studied $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts prepared by wet impregnation and grafting methods. They observed that as V_2O_5 concentration was increased, the XPS V $2p_{3/2}/\text{Ti } 2p_{3/2}$ intensity ratio increased to approximately 7 wt.%, but after two monolayers were deposited the ratio remained approximately constant. These results suggest that once the V_2O_5 amount exceeds that necessary for formation of the first monolayer, the V_2O_5 is not dispersed uniformly, but crystallites of V_2O_5 cover a fraction of the monolayer surface. Based on XPS, XRD, IR, and NMR vanadium oxide is present as monomeric species as the loading increase, polymeric forms of vanadium oxide are present and at 25 wt.% crystalline form of V_2O_5 are present.

Structure of Reacted Vanadium/Aluminum Antimonate Catalysts. The V/Al XPS intensity ratios for the reacted samples suggest that the dispersion of the vanadium does not change under reaction conditions. In order to determine if XPS can distinguish between V^{5+} and V^{4+} the binding energies of standard compounds have been obtained. Unfortunately, the binding energies of standard compounds have shown that it is difficult to distinguish between V^{5+} and V^{4+} . However, as seen from Figure 3.4, slight changes in the position of the vanadium peak for the powder, spray coated, propylene/ O_2/He , and O_2/He occurs, but the shifts observed are not as large as expected for a change in the vanadium oxidation state. The V $2p_{3/2}$ binding energies reported in the literature for V_2O_5 vary from 516.4 to 517.4 eV [23,24]. For V^{4+} , represented by V_2O_4 , the binding energies range from 515.4 to 515.7 eV [25,26]. Based on literature values, it appears that the vanadium in the catalyst is V^{5+} . Unfortunately, XPS cannot unequivocally determine if a change in vanadium oxidation state occurs due to reaction.

EPR spectra clearly show that some of the vanadium is reduced from V^{5+} to V^{4+} under reaction conditions. Because of the high concentration of vanadium present in this system, it is not possible to obtain any useful information from the hyperfine splitting of the catalyst series. With conventional EPR, noise caused by the cavity was seen and at lower concentrations this signal was greater than that of the signal due to the vanadium. Thus, at present, we cannot obtain coordination of the vanadium as a function of loading and we cannot obtain quantitative information about the amount of reacted vanadium.

Influence of Catalyst Structure on Activity and Selectivity. The V5 catalyst shows the greatest selectivity towards acrolein production. With the conversion extremes similar, the selectivity toward acrolein for the monomeric form is still greater than that with crystalline forms present. In addition, the pure aluminum antimonate support produced higher levels of carbon oxides than the promoted support. Activity measurements of the vanadium/aluminum antimonate catalyst suggest that monomeric forms of vanadium oxide are more selective in the production of acrolein than polymeric and crystalline forms of vanadium oxide. However, all forms of supported vanadium oxide catalysts showed greater selectivity toward acrolein than the aluminum antimonate support.

By the addition of vanadium to the surface of the support, a redox element having a $V=O$ bond is present. The presence of a terminal $V=O$ site, the selectivity during the oxidation process has been shown to be effected [27]. It is generally believed that too weak $M-O$ bonds results in non-discriminative $C-O$ bond formation which leads to combustion. If the $M-O$ bond is too strong, lattice oxygen is unavailable to participate in the reaction [28]. In addition to $M=O$ bonds and bond strength, geometric effects also play a role in that the active site must contain "the right amount" of oxygen [29]. In this system, the presence of the vanadium increases the selectivity to acrolein at all active phase loadings. However, as crystalline phases of V_2O_5 become present, an increase in CO_x and the by-product, acetaldehyde is observed. This may be due to the reactive nature

of crystalline phases. In this system, as with MoO_3 -based mixed oxide catalysts, it is possible that the rate of allylic oxidation is controlled by the rate of allylic-intermediate formation [30].

Straguzzi et al. [31] studied the conversion of 1-butene to butadiene on aluminum antimonate catalyst and found that the selectivity to butadiene was 75% at conversions less than 25% and showed activity of 1.0 mmol/m²h. Straguzzi suggests that due to the difficulty in reducing Al^{3+} , the activity of the aluminum antimonate can be attributed to Sb cations. However, the aluminum antimonate they prepared had a surface area of 51 m²/g and was higher in crystallinity. The aluminum antimonate that was produced in this work demonstrated a low selectivity to acrolein, 59.5%.

The structure of the antimonate site for selective oxidation in uranium antimonate is composed of bridging oxygen species which connect two Sb^{5+} and two Sb^{3+} atoms. In this, the Sb^{3+} -O bridge serves as the H abstracting species and gives radical character to the oxygen bond at the site. This facilitates the H abstraction. The Sb^{5+} -O moieties are used as olefin chemisorption sites and sites for the insertion of oxygen [32]. In order to determine which of these processes are occurring, further investigation is needed.

3.5. Conclusions

The combined use of several techniques to investigate the structure and dispersion of V/AlSbO₄ catalysts leads to the following conclusions:

1. XPS, XRD, IR, and NMR data indicates that AlSbO₄ is a pure phase with no formation of aluminum or antimony oxide species present.
2. XPS, XRD, and IR data indicate that V is highly dispersed over the AlSbO₄ carrier. XRD and XPS results suggest the trend of crystallite formation is consistent with estimated monolayer capacity calculations.

3. Based on XPS, data both Sb and V species are in the +5 oxidation state. XPS binding energies of V and Sb do not change as a function of loading or reaction conditions.

4. IR and NMR data suggest that the vanadium oxide does not form a vanadate-type structure with the aluminum antimonate support.

5. EPR data indicates that vanadium is reduced from V^{5+} to V^{4+} during propylene oxidation.

6. Activity data suggests that low loadings of vanadium oxide ($V/Al \leq 0.26$) increase selectivity to acrolein. Pure aluminum antimonate support shows lower selectivity to acrolein than vanadium oxide supported catalysts at all loadings.

References

1. F. J. Berry and M. E. Brett, *J. Catal.*, **88**, 232, (1984).
2. G. Centi, D. Pesheva, and F. Trifirò, *Appl. Catal.*, **33**, 343, (1987).
3. G. Centi, R. K. Grasselli, E. Patane, and F. Trifirò, in "New Developments in Selective Oxidation", *Stud. Surf. Sci. Catal.*, **55**, (1990).
4. P.G. Pries DE Oliveira, F. Lefebvre, M. Primet, J.G. Eon, and J.C. Volta, *J. Catal.*, **130**, 293, (1991).
5. P.G. Pries DE Oliveira, J.G. Eon, and J.C. Volta, *J. Catal.*, **137**, 257, (1992).
6. H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials", New York, N.Y., Wiley-Interscience Publication, 1974.
7. A. Proctor, University of Pittsburgh.
8. C. Defosse, P. Canesson, P. G. Rouxlet, and B. Delmon, *J. Catal.*, **51**, 269, 1979.
9. F. P. J. M. Kerkhof and J. A. Moulijn, *J. Phys. Chem.*, **83**, 1612, 1979.
10. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 129, 1979.
11. D. R. Penn, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 29, 1976.
12. D.V. Tarasova, V.A. Dzis'ko, I.P. Olen'kova, L.T. Tsikza, L.G. Karakchiev, and V.V. Molodtsova, *Kin. i Kata.*, **14**(2), 481, 1973.
13. Y. Nakagawa, T. Ono, H. Miyata, and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. I*, **79**, 2929, 1983.
14. H. Eckert and I.E. Wachs, *J. Phys. Chem.*, **93**, 6796, 1989.
15. G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, Wiley, New York, 1987.
16. P. Massiani, B. Chauvin, F. Fajula, F. Figueras, and C. Gueguen, *Appl. Catal.*, **42**, 105, 1988.

17. P.G. Pries de Oliveria, F.Lefebvre, M. Primet, J.G. Eon, and J.C. Volta, *J. Chem. Soc., Chem. Commun.*, 1480, 1990.
18. F. Roozeboom, T. Fransen, P. Mars, and P.J. Gellings, *Anorg. Allg. Chem.*, **449**, 25, 1979.
19. A.A. Davydov, *Zh. Fiz. Khim.*, **65**, 1803, 1991.
20. H. Miyata, K. Fujii, T. Ono, Y. Kubokawa, T. Ohno, and F. Hatayama, *J. Chem. Soc., Faraday Trans.*, **83**(1), 675, 1987.
21. Y. Kera and K. Hirata, *J. Phys. Chem.*, **37**(11), 3973, 1969.
22. G. Bond and P. König, *J. Catal.*, **77**, 309, 1982.
23. G.C. Bond, J.P. Zurita, and S. Flamerz, *Appl. Catal.*, **27**, 353, 1986.
24. B. Blaauw, F. Leenhouts, F. van der Woude, and G.A. Sawatsky, *J. Phys. C.*, **8**, 367, 1975.
25. J. Mendialdua, Y. Barbaux, L. Gengembre, J.-P. Bonnelle, B. Grzybowska, and M. Gasior, *Bull. Pol. Acad. Sci. Chem.*, **35**, 213, 1987.
26. B. Blaauw, F. Leenhouts, F. van der Woude, and G.A. Sawatsky, *J. Phys. C.*, **8**, 367, 1975.
27. K. Mori, Y. Yoda, N. Tamazoe, and T. Seiyona, *J. Phys. Chem.*, **84**, 2564, 1984.
28. W.M.H. Sachtler, G.J.H. Dorgels, V. Farenfort, and R.J.H. Voorhoeve, *Proc. 4th Intern. Cong. Catal.*, **1**, 355, 1970.
29. R.K. Grasselli, *Appl. Catal.*, **15**, 127, 1985.
30. H.H. Voge and C.R. Adams, "Advances in Catalysis", Vol. 17, p. 151, Academic Press, New York, 1967.
31. G.I. Straguazzi, K.B. Bischoff, T.A. Koch, and G.C.A. Schuit, *J. Catal.*, **104**, 47, 1987.
32. J.D. Burrington, C.T. Kartisek, and R.K. Grasselli, *J. Catal.*, **87**, 363, 1984.

Chapter 4

Supported Antimony Oxide Catalysts

4.1. Introduction

Antimony oxide is often employed to promote the activity of catalysts used for selective oxidation [1-5] and for related reactions such as oxidative coupling [6]. Among the more common reactions are the oxidation and ammoxidation of propylene to acrolein and acrylonitrile, the conversion of isobutene to methacrolein, and the condensation of isobutene and formaldehyde to isopropene.

Grasselli and co-workers [7] examined the relationship between structure and catalytic activity of uranium-antimonates for the synthesis of acrylonitrile from propylene, ammonia, and air. They found that USbO_5 and $\text{USb}_3\text{O}_{10}$ phases are catalytically active, but only $\text{USb}_3\text{O}_{10}$ is selective. The selectivity has been attributed to the orthorhombic structure that has no adjacent U-O-U structures. In USbO_5 , U-O-U-O-U structures present in the catalyst are centers for waste formation.

In addition, work has been performed on iron antimonate catalysts which are used for the conversion of butene into butadiene [8-14]. Numerous hypotheses have been proposed to explain the reactivity of Fe-Sb-O systems based on surface geometry, electronic properties, and bulk structure [10,11,13]. Considerable work has also been performed on Sb oxides supported on rutile structures such as SnO_2 [15-18] and TiO_2 [19] for the selective oxidation of propylene to acrolein. It appears that in these systems, the catalytic performance for the oxidation of olefins is related to an enhancement of antimony at the surface of the rutile support. This enhancement is achieved by high temperature calcination which results in migration of the antimony through the bulk.

Lo et al. [20] reported the oxidative coupling of methane using a potassium-modified silica supported antimony oxide catalyst. This study found that of the Sb_6O_{13} , KSbO_3 , and $\alpha\text{-Sb}_2\text{O}_4$ phases most predominantly formed, only $\alpha\text{-Sb}_2\text{O}_4$ was selective in methane oxidative coupling reactions and gave high selectivity to C_2 .

Antimony oxide has also been used as a promoter for catalysts used in CO oxidation [21]. Ali-Zade et al. [22] found that the activity of Cu, Co, Cr, and Mn oxides supported on γ -alumina is improved when Sb oxide is added. Antimony oxides have also been used in conjunction with oxides of Be, Mg, Zn, Al, Si and rare earth metals [23] and Sn-Mn-Pb oxides [24] for treatment of exhaust gases.. Straguzzi et al. [8,10] examined CO oxidation and selective oxidation of 1-butene to butadiene on iron, aluminum, cobalt, chromium, and rhodium antimonates. They found that these reactions have the same trend in activity, which suggests that the reactions occur on the same site and indicates that the antimony serves two functions: 1) to limit the size of the active oxygen ensemble and 2) to adsorb O_2 .

In recent years, there has been an increased interest in preparation methods to produce highly dispersed metal oxides on supports such as SiO_2 , Al_2O_3 , and TiO_2 [25,26]. In general, these procedures are directed at producing monolayers with high thermal stability of the metal oxide coating. However, it has been found that the sorption [27,28] and catalytic properties [29-31] of the monolayer metal oxides are often different from those observed for the unsupported oxide phase. For example, Denofre et al. [28] found that $\text{Nb}_2\text{O}_5/\text{SiO}_2$ irreversibly adsorbs ascorbic acid forming a surface complex. Shirai et al. [29] reported that the activity of $\text{Nb}_2\text{O}_5/\text{SiO}_2$ was 20 times greater than niobic acid bulk catalysts for esterification from ethanol and acetic acid.

Recently, Benvenutti et al. [32] have reported the thermal stability and the acidic properties of Sb_2O_5 grafted on silica. Their results suggest that when antimony atoms are distant thermal sintering occurs formation of crystalline Sb_2O_5 is inhibited. The highly dispersed material contains Lewis acid sites due to unsaturated coordination of the Sb^{5+}

ion. The sites disappear upon thermal treatment at 500°C due to the extensive reticulation of Sb^{5+} with the silica surface.

In this chapter, the surface structure of silica and alumina supported antimony oxide catalysts will be correlated with their activity for CO oxidation. The focus will be on defining the nature of the Sb-support interaction and the influence of Sb dispersion and reactivity on the catalytic properties of the mixed oxides. In order to determine structure and reactivity of the species in the mixed oxide catalysts, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) will be used. The results obtained will be correlated with CO oxidation activity measurements in order to establish the nature of CO oxidation site(s) in the supported Sb oxide catalysts.

4.2. Experimental

Catalyst Preparation. The supported antimony oxide catalysts were prepared by pore volume impregnation of $\gamma\text{-Al}_2\text{O}_3$ (Cyanamid; surface area: 204 m^2/g ; pore volume: 0.6 ml/g) and SiO_2 (Davison; surface area: 310 m^2/g ; pore volume: 1.15 ml/g) which had been ground to 230 mesh. The supports were calcined in air at 500°C for 12 hours. The SiO_2 was allowed to sit in a desiccator for 12 days and Al_2O_3 for 7 days prior to impregnation. The catalysts were prepared by incipient wetness using a solution of antimony (III) n-butoxide (Strem, 99%) in dry n-hexane (Aldrich, 99.9%). The impregnated catalysts were dried at room temperature in a nitrogen atmosphere for 48 hours, dried in air at 120°C for 24 hours and then calcined in air at 500°C for 12 hours. Nominal loadings of the active element range from 0–40 wt.% as Sb_2O_5 (Sb/Al atomic ratio of 0 to 0.21 and Sb/Si atomic ratio of 0 to 0.25). Catalysts will be designated as Sb#Al for the Sb/ Al_2O_3 series and Sb#Si for the Sb/ SiO_2 series where # is the weight percent of antimony as Sb_2O_5 .

Standard Materials. Sb_2O_5 was prepared by the addition of SbCl_5 to deionized water under vigorous stirring. The pH of the solution was then adjusted to a pH of 6-7. The precipitate formed was filtered and washed with deionized water, dried in air at 120°C for 12 hours and calcined at 500°C for 12 hours. AlSbO_4 was prepared by coprecipitation of a 1:1 atomic ratio of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (J.T. Baker, A.C.S. grade) dissolved in deionized water and SbCl_5 (Aldrich, 99%). SbCl_5 was added to a vigorously stirred solution of $\text{Al}(\text{NO}_3)_3$ over a 30 minute period. NH_4OH (J.T. Baker, A.C.S. grade) was added until the solution pH reached 6-7. The neutralized solution was allowed to stir for 1 hour. The precipitate formed was filtered and washed with deionized water; dried in air at 120°C for 12 hours, ground to produce a homogeneous mixture, and calcined at 750°C for 12 hours. XRD patterns of the standard compounds matched the appropriate ASTM powder diffraction file.

BET Surface area. Surface area measurements were determined using a QuantaChrome Quantasorb Jr. Sorption System. Approximately 0.1 grams of the catalyst was outgased between 160°C - 165°C for 12 hours prior to adsorption measurements. The measurements were made using relative pressures of N_2 to He of 0.05, 0.08, and 0.15 (surface area N_2 : 0.162 nm^2) at 77 K. Data were processed using a Macintosh computer.

X-ray Diffraction. XRD patterns were obtained using a Rigaku XRD diffractometer which employs $\text{Cu K}\alpha$ radiation ($1.541838 \text{ \AA}$). The x-ray was operated at 45 kilovolts and 100 milliamps. The patterns were scanned between 10° - 75° (2 theta) for Al_2O_3 catalysts and 10° - 45° (2 theta) Sb/SiO_2 catalysts. The scan rate was $0.1^\circ/\text{min}$. with DS and SS = 0.5. Powdered samples were mounted on glass slides by pressing the powder in an indentation on one side of the slide. Semi-quantitative XRD has been performed by using physical mixtures of Sb_2O_5 and Al_2O_3 with 0.05 wt %, 0.1 wt %, 0.25 wt %, and 0.5 wt % Sb_2O_5 . For Sb/SiO_2 , physical mixtures of Sb_2O_5 and SiO_2 with 0.25 wt.%, 0.45 wt.%, and 0.7 wt.% Sb_2O_5 were prepared. The samples were ground in order to produce a homogenous mixture. The areas of the Sb_2O_5 $\langle 400 \rangle$ and the Al_2O_3

<400> or SiO_2 <101> peaks were measured and used to generate a calibration curve that can be used to determine the amount of crystalline Sb_2O_3 present in the $\text{Sb}/\text{Al}_2\text{O}_3$ or Sb/SiO_2 catalysts. Peak areas were obtained using Googly software [33] and a linear background was assumed over the peak base.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectra (XPS) were obtained using a Perkin-Elmer spectrometer equipped with a Mg (1253.6 eV)/Al (1486.6 eV) dual anode and a 10-360 hemispherical analyzer with an omnifocus small spot lens. Data were collected using a PC 137 interface board and a Zeos 386SX computer. Samples were mounted as powders on double-sided sticky tape or spray coated on glass slides or stainless steel plates. Spray coated samples were prepared by air brushing a 10% suspension of the catalyst (20% deionized water and 80% acetone) onto a glass slide or a stainless steel plate heated at 60°C. XPS binding energies of the $\text{Sb}/\text{Al}_2\text{O}_3$ catalysts were referenced to the Al 2p (74.5 eV) and Sb/SiO_2 catalysts to the Si 2p (103.5 eV) peak. The binding energies for standard compounds were referenced to the C 1s (284.6 eV) peak. XPS binding energies were measured with a precision of ± 0.2 eV, or better. The data were processed using Googly software.

In situ XPS experiments were performed on catalysts treated in a reaction chamber attached to the spectrometer and transferred directly to the analysis chamber without exposure to air. The antimony oxide catalysts were reacted with 100 cc/minute of 5% O_2 and 95% He for 1 hour at 350°C, then reacted in 20 cc/minute of H_2 at 450°C for 10 minutes and then for 10 minutes at 450°C with 20 cc/minute of O_2 .

Quantitative XPS. A number of models have been proposed to relate active phase/support XPS peak intensity ratios to catalyst structure. It has been shown by Defosse et al. [34] that one can calculate the theoretical intensity ratio (I_p^0/I_s^0) expected for a supported phase (p) atomically dispersed on a carrier (s). Kerkhof and Moulijn [35] extended the Defosse model and derived expressions based on model catalysts that consist of sheets of support with cubic particles of active phase deposited between the support

layers. The photoelectron cross-sections (σ) and mean escape depths (λ) of the photoelectrons used in the calculations are taken from Scofield [36] and Penn [37], respectively. For species dispersed as monolayers, the relationship is given by the following equation:

$$\left(\frac{I_p^0}{I_s^0} \right)_{\text{monolayer}} = \left(\frac{p}{s} \right)_b \frac{D(\epsilon_p) \sigma_p \beta_1 (1 + e^{-\beta_2})}{D(\epsilon_s) \sigma_s 2(1 - e^{-\beta_2})} \quad (2)$$

where I_p^0 is the intensity of the electrons from element p in the supported phase, I_s^0 is the intensity of electrons from element s in the carrier, σ_p and σ_s are photoelectron cross sections of the respective elements, $D(\epsilon_{p,s})$ are detector efficiencies, $\epsilon_{p,s}$ are the kinetic energies of the electrons, and $\beta_{1,2}$ is the thickness (t) per the mean escape depth of the photoelectron from the support (λ_s) or the promoter (λ_p). This model predicts a linear increase in the supported phase (p) to the carrier (s) peak intensity ratio as the (p/s) atomic ratio is increased.

CO Oxidation. CO oxidation experiments were carried out in a differential type flow reactor at low conversions (<10%). Steady-state was reached between 1.5 and 2 hours for each catalyst series. The gas flow rates were held constant with Brooks 5850 and Porter 201 mass flow controllers. The reactor temperature was monitored with an Omega CN 1200 controller. The gas products for Sb/Al₂O₃ and SiO₂ were analyzed with a Varian 920 gas chromatograph equipped with a TCD. The chromatograph was interfaced to a Hewlett-Packard 3394A integrator. The column used for permanent gas separation was a 5 foot 60/80 mesh Carbosieve column. The catalysts were pretreated with 5% O₂ (99.98%)/95% He (99.9%) at 350°C for 1 hour prior to reaction. The

reactor was operated at 450°C with a 15 cc/minute flow of 4.8% CO/9.8% O₂/85.4% He (mixture from AGA with purity > 99.9%).

4.3. Results

BET. Variation in the BET surface area of Sb/Al₂O₃ and Sb/SiO₂ catalysts as a function of antimony oxide content are shown in Table 4.1. For both series, the surface area decreases as the loading of the antimony increases. However, corrections made for the active phase loading indicate that the surface area of the support does not change.

X-ray Diffraction (XRD). XRD patterns measured for the Sb/Al₂O₃ catalysts showed lines characteristic of the alumina carrier (Figure 4.1). For Sb₂O₅ loadings ≤ 15 wt.% only peaks of the alumina carrier were seen. For loadings ≥ 20 wt.% a new feature is observed between 20–40° (2 theta). The feature is centered at approximately 29° (2 theta) for all loadings. As the Sb₂O₅ loading increases, the intensity of this feature increases. At loadings of 35 and 40 wt.% Sb₂O₅, Sb₂O₅ <400> and Sb₂O₅ <111> peaks are observed. Figure 4.2 shows the variation of the Sb₂O₅ <400>/Al₂O₃ <400> intensity ratios measured for Sb₂O₅/Al₂O₃ physical mixtures. The value measured for the Sb40Al catalyst is also given. The results indicate that the amount of Sb₂O₅ crystallite in the catalyst is less than 0.2 wt.% Sb₂O₅.

XRD patterns measured for the Sb/SiO₂ catalysts show the broad peak centered at 22° (2 theta) characteristic of the silica carrier (Figure 4.3). For Sb₂O₅ loadings less than 10 wt.% only the peak from the silica support was observed. For Sb₂O₅ loadings > 10 wt.% a new feature between 20° and 40° (2 theta) is observed centered at approximately 29° (2 theta). As the loading of Sb₂O₅ increases, the intensity of this feature increases. At loadings of 25, 35, and 40 wt.% Sb₂O₅, Sb₂O₅ <400> and Sb₂O₅ <111> peaks are observed. Figure 4.4 shows the variation of the Sb₂O₅ <400>/SiO₂ <101> intensity ratios measured for Sb₂O₅/SiO₂ physical mixtures. The results indicate that the amount of

Table 4.1. BET surface area (m²/g) of Sb₂O₅/Al₂O₃ and SiO₂.

Weight % Sb ₂ O ₅	Al ₂ O ₃	SiO ₂
0	203.6	307.8
5	195.2	285.5
10	179.5	261.1
15	172.5	241.3
20	167.5	228.3
25	162.7	210.1
30	149.1	198.9
35	135.8	175.2
40	129.1	163.4

Sb_2O_5 crystallite in each catalyst is less than 0.5 wt.% Sb_2O_5 .

The presence of XRD peaks due to Sb_2O_5 observed for high Sb loadings can be attributed to errors in catalyst preparation. During the preparation of Sb rich catalysts ($\text{Sb}_2\text{O}_5 > 20$ wt.%) it is likely that very small amounts of the antimony alkoxide migrates out of the catalyst bed onto the walls of the crucible used to prepare the catalysts. During calcination the alkoxide is converted to Sb_2O_5 which subsequently falls into the catalyst bed. Unfortunately, the crystallites are not large enough to be separated by sieving. Thus, we believe that much of the crystalline Sb_2O_5 observed in the catalyst is due to this preparation error. Samples were prepared three times in an effort to eliminate this problem. Results are presented for the samples that gave the lowest Sb_2O_5 $<400>$ XRD peak intensity.

The XPS Sb $3d_{3/2}$ binding energies measured for the powder, spray coated and reacted $\text{Sb}/\text{Al}_2\text{O}_3$ and Sb/SiO_2 catalysts were 540.6 ± 0.2 eV. The XPS Sb $3d_{3/2}$ binding energy measured for Sb_2O_5 was 540.5 eV. The XPS Sb $3d_{3/2}$ binding energy measured for AlSbO_4 was 540.5 eV.

Figure 4.5 shows the variation of the Sb $3d_{3/2}$ /Al 2p intensity ratio as a function of the Sb/Al atomic ratio measured for the $\text{Sb}/\text{Al}_2\text{O}_3$ catalysts. For Sb_2O_5 loadings < 30 wt.% the intensity ratios increase linearly with Sb loading for powder, spray coated, and reacted samples. For loadings ≥ 35 wt.% the increase in Sb/Al intensity ratios with Sb loading is less pronounced. Variation of the Sb $3d_{3/2}$ /Si 2p XPS intensity ratio as a function of the Sb/Si atomic ratio is shown for the Sb/SiO_2 catalysts in Figure 4.6. There is a linear increase in Sb/Si intensity ratio as a function of Sb loading for powder, spray coated, and reacted samples.

CO Oxidation Activity. Table 4.2 shows the average percent conversion for $\text{Sb}/\text{Al}_2\text{O}_3$ and Sb/SiO_2 catalyst series. For the $\text{Sb}/\text{Al}_2\text{O}_3$ catalysts, the percent CO conversion increases with Sb loading up to the Sb15Al catalyst. The activity decreases as the Sb loading increases from 15 to 40 wt.% Sb_2O_5 . For Sb loadings ≥ 25 wt.% Sb_2O_5 ,

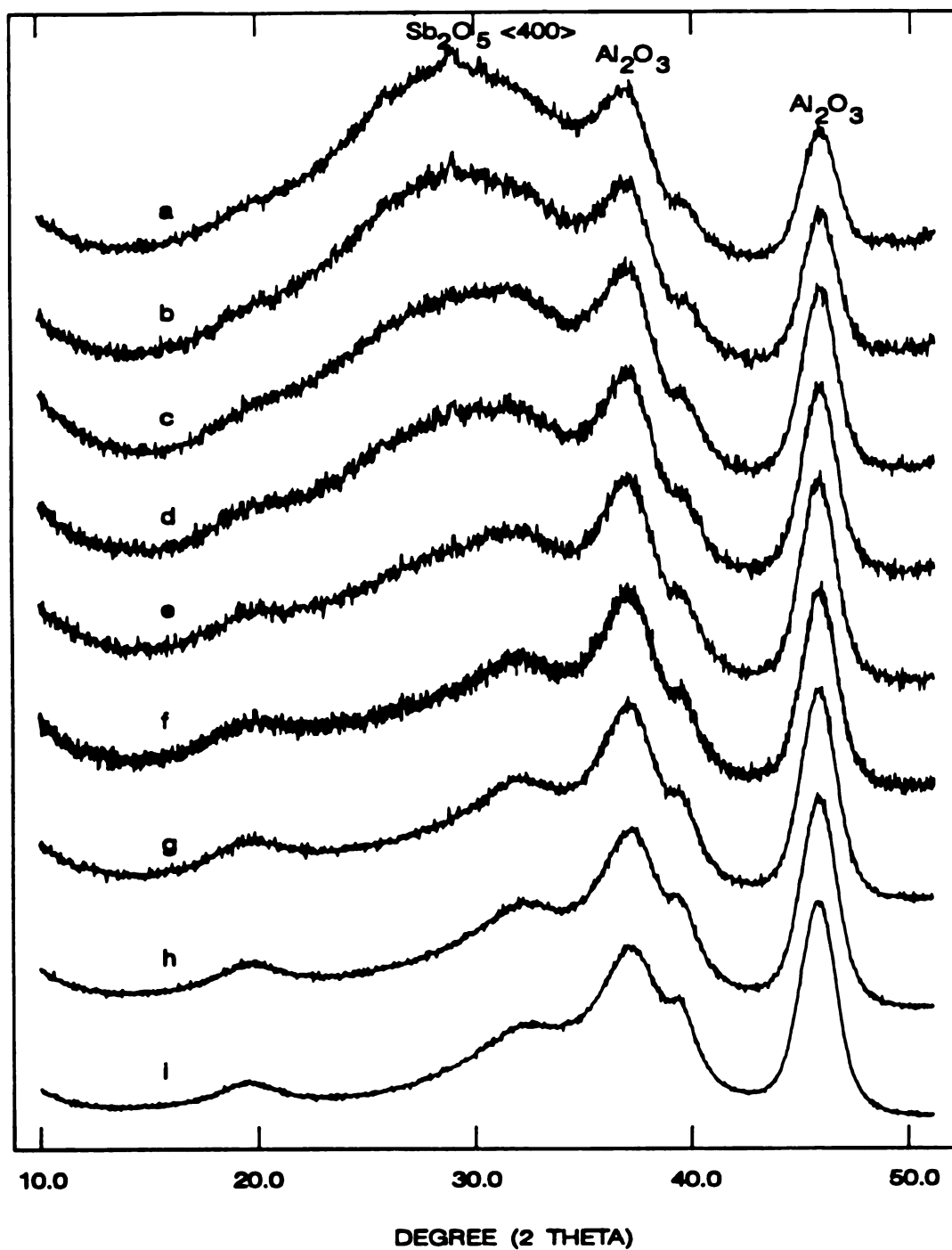


Figure 4.1. XRD of $\text{Sb}_2\text{O}_5/\text{Al}_2\text{O}_3$ a) Sb_{40}Al , b) Sb_{35}Al , c) Sb_{30}Al , d) Sb_{25}Al , e) Sb_{20}Al , f) Sb_{15}Al , g) Sb_{10}Al , h) Sb_5Al , and i) Sb_0Al catalysts.

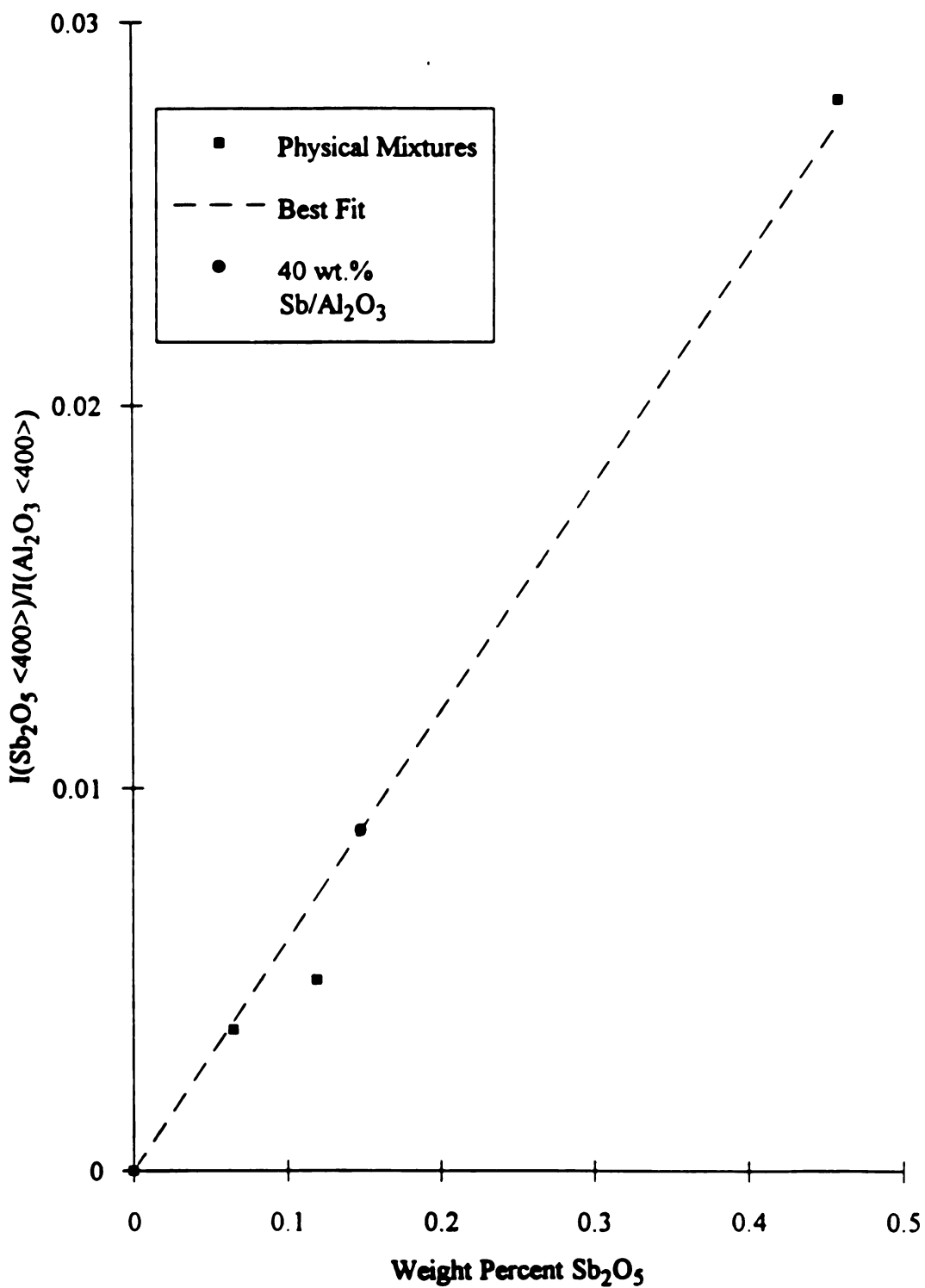


Figure 4.2. Semi-quantitative XRD physical mixtures of Sb_2O_5 and Al_2O_3 .

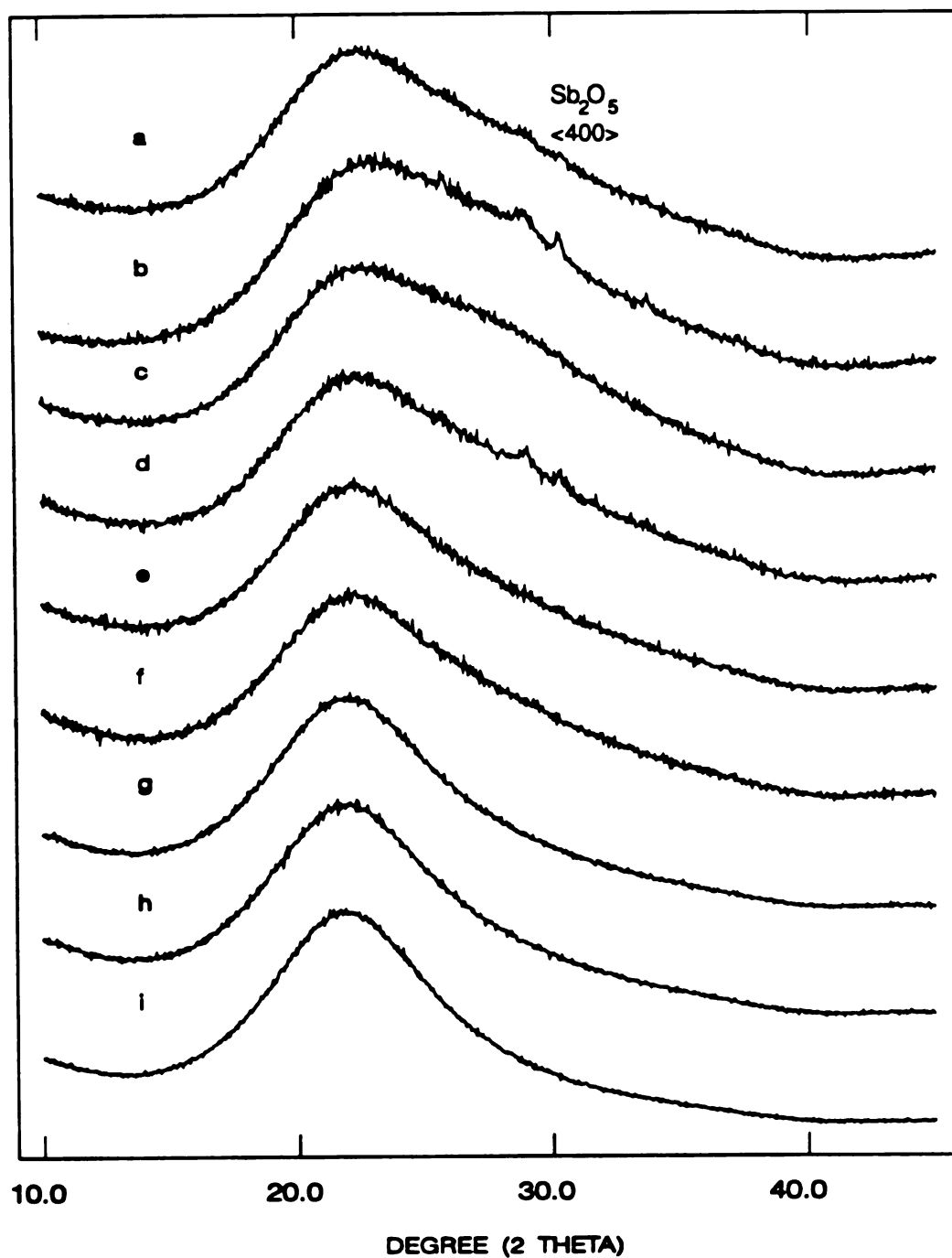


Figure 4.3. XRD of $\text{Sb}_2\text{O}_5/\text{SiO}_2$ a) Sb40Si, b) Sb35Si, c) Sb30Si, d) Sb25Si, e) Sb20Si, f) Sb15Si, g) Sb10Si, h) Sb5Si, and i) Sb0Si catalysts.

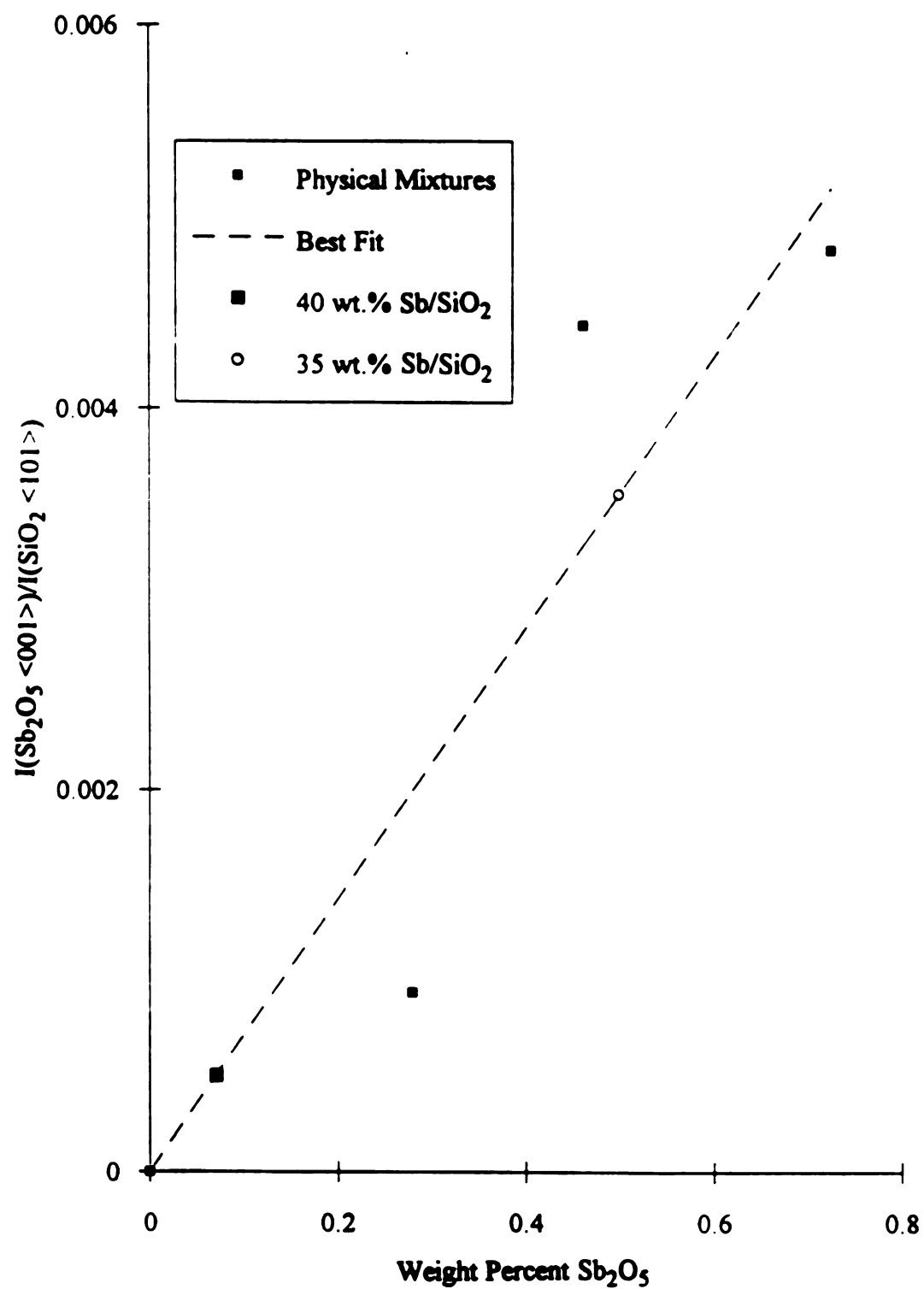


Figure 4.4. Semi-quantitative XRD physical mixtures of Sb_2O_5 and SiO_2 .

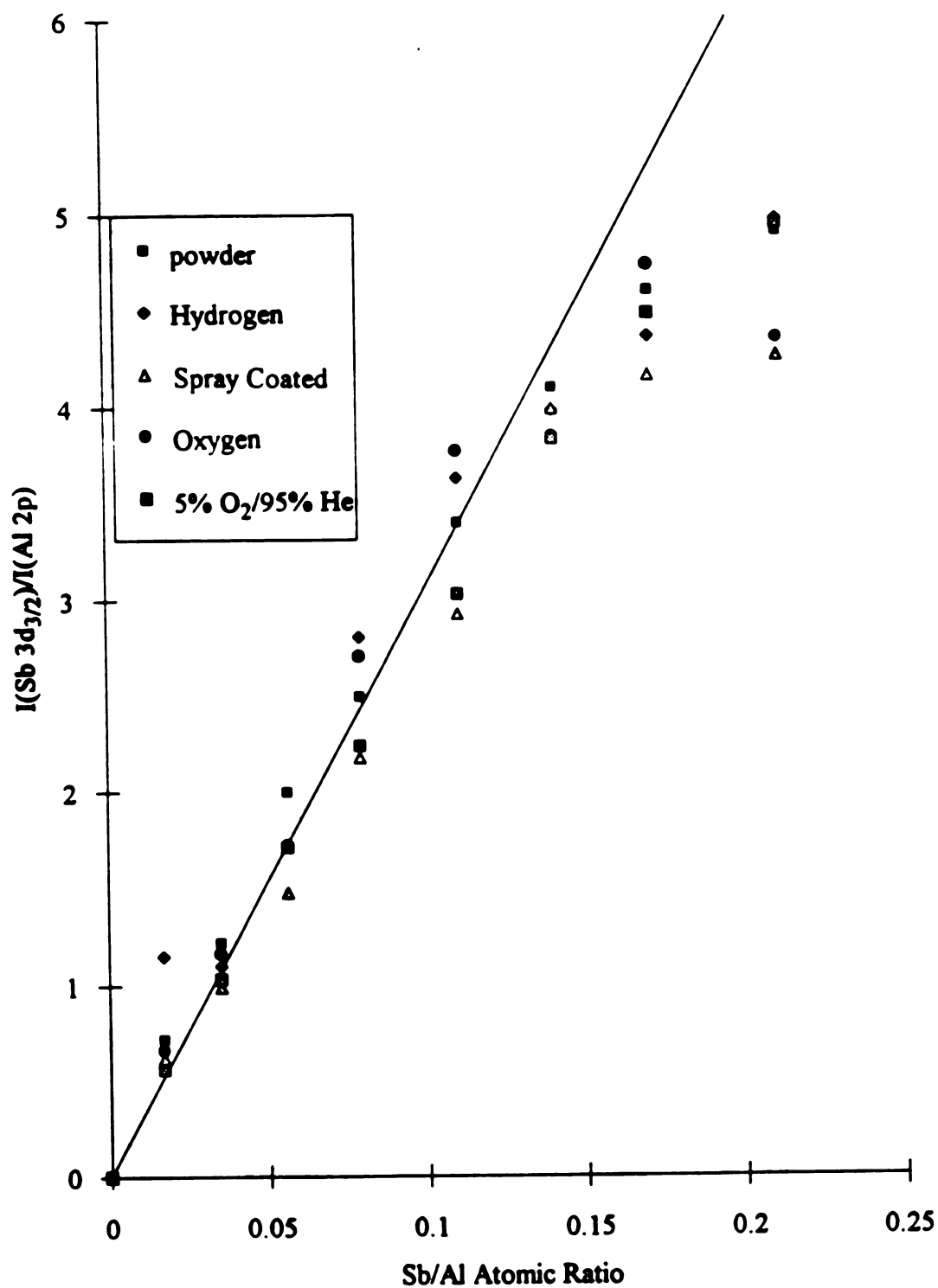


Figure 4.5. XPS intensity ratio of Sb $3d_{3/2}$ /Al 2p as a function of Sb/Al atomic ratio.

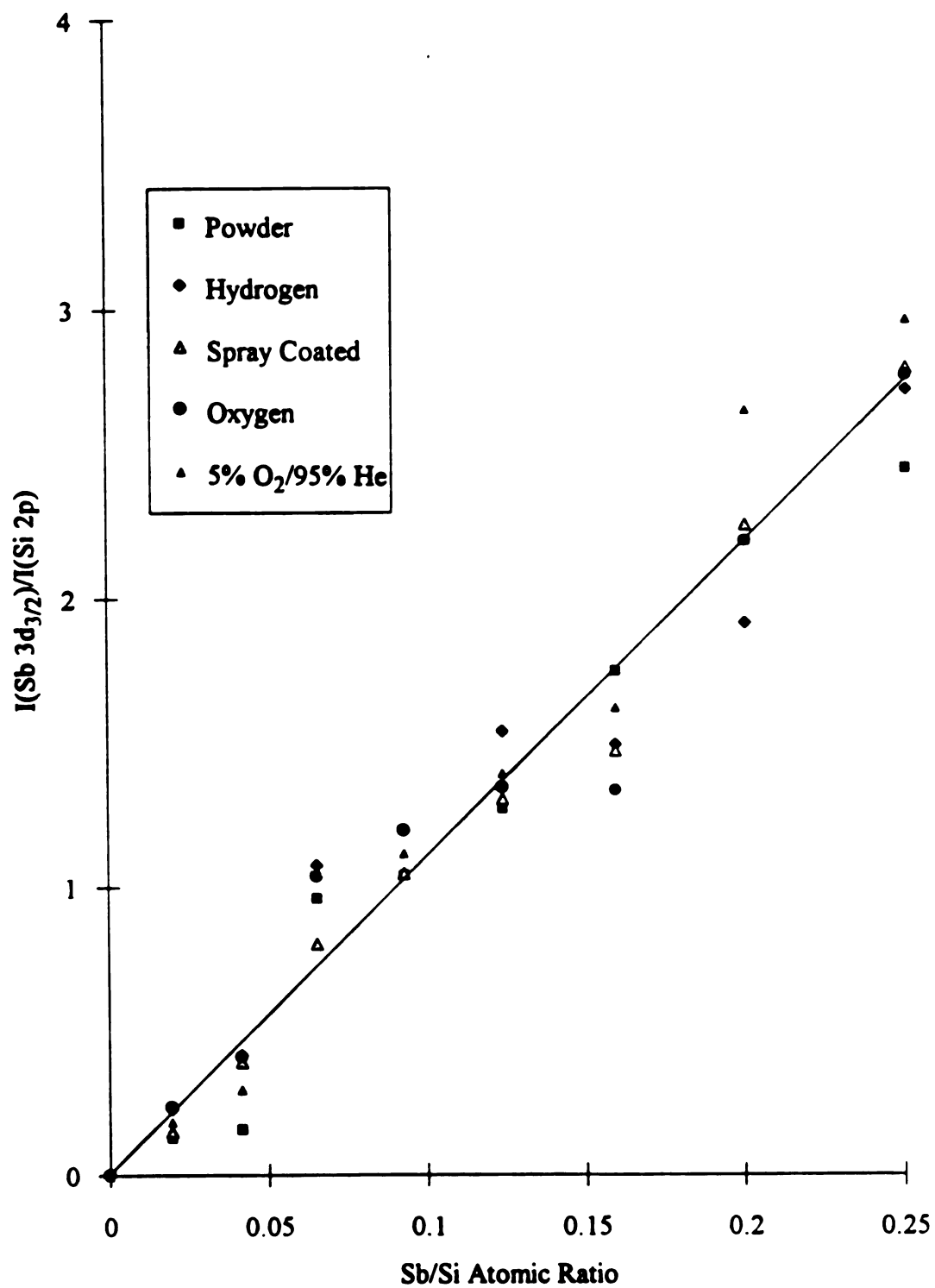


Figure 4.6. XPS intensity ratio of Sb 3d_{3/2}/Si 2p as a function of Sb/Si atomic ratio.

Table 4.2. CO conversion for $\text{Sb}_2\text{O}_3/\text{Al}_2\text{O}_3$ and $\text{Sb}_2\text{O}_3/\text{SiO}_2$ at 450°C and 15 cc/minute flow rate.

Weight % Sb_2O_3	Percent Conversion for $\text{Sb}/\text{Al}_2\text{O}_3^{\text{a}}$	Percent Conversion for $\text{Sb}/\text{SiO}_2^{\text{a}}$
0	2.7	0.4
5	5.1	1.1
10	7.0	2.0
15	7.3	1.3
20	4.0	1.9
25	2.2	0.9
30	1.8	0.9
35	1.7	0.8
40	1.0	0.8
AlSbO_4	9.6	—

^a - Error bars of $\pm 10\%$.

the activity is lower than the value obtained for the support.

For the Sb/SiO₂ catalysts, the percent CO conversion increases with Sb loading up to the Sb₂₀Si catalyst. The activity decreases as the Sb loading increases from 20 to 40 wt.% Sb₂O₅. As shown from the table the activity of antimony oxide supported on alumina is greater than that of the silica. However, the two series show similar trends in the region of greatest activity (between 10 and 20 wt.% Sb₂O₅). CO oxidation was performed using the AlSbO₄ catalyst. The average percent conversion at steady state is 9.6%.

4.4. Discussion

Structure of Calcined Antimony Oxide/Alumina Catalysts. For Sb/Al₂O₃ catalysts with Sb₂O₅ loadings ≤ 30 wt.%, absence of peaks that can be attributed to any antimony oxide phases indicates that no crystalline antimony oxide phases are formed in these catalysts. However, the observation of the Sb₂O₅ <400> peak for catalysts with ≥ 35 wt.% Sb₂O₅ indicates crystalline Sb₂O₅ is present. Semi-quantitative XRD analysis suggests that these catalysts contain less than 0.2% crystalline Sb₂O₅. In addition, the broad peak centered at approximately 29° (2 theta) is in the same region of the crystalline Sb₂O₅ <400>. This may be attributed to an amorphous form of antimony oxide. The XPS Sb 3d_{3/2} binding energies measured for Sb/Al₂O₃ catalyst series indicates that the antimony is in the +5 oxidation state and does not vary as a function of antimony loading.

The XPS Sb/Al intensity ratios measured for the alumina catalysts with ≤ 30 wt.% Sb₂O₅ show a linear increase in intensity ratio as the Sb/Al atomic ratio increases. This suggests that the antimony phase is well dispersed over the alumina carrier up to 30 wt.%. For higher Sb loadings, the deviation from linearity indicates that the antimony oxide is not as highly dispersed over the alumina support. This is consistent with XRD results.

Further, the absence of any significant change in Sb/Al intensity ratio following reactions suggests that the antimony oxide phase is not mobile under reaction conditions.

Structure of Calcined Antimony Oxide/Silica Catalysts. For Sb/SiO₂ catalysts with ≤ 30 wt.% Sb₂O₅, the absence of peaks that can be attributed to antimony oxide phases indicate that no crystalline forms of antimony oxide are present. However, the observation of Sb₂O₅ <400> peak for catalysts with 25 wt.% and ≥ 35 wt.% Sb₂O₅ indicates that crystalline Sb₂O₅ is present. In addition, the broad peak centered at approximately 29° (2 theta) is in the same region of the crystalline Sb₂O₅ <400>. This result indicates that an amorphous form of antimony oxide is produced on the support. The XPS Sb 3d_{3/2} binding energies measured for Sb/SiO₂ catalyst series indicates that the antimony is in the +5 oxidation state and is independent of antimony loading. Binding energies for the series are similar to those reported previously [38,39].

For Sb/SiO₂ catalysts, the linear increase in Sb/Si XPS intensity ratio with increasing Sb loading suggests that antimony oxide is highly dispersed. This is consistent with XRD results which showed a broad feature that we have attributed to dispersed antimony oxide. In addition, no change is observed under reaction conditions. This indicates that the reactions do not affect the dispersion of the antimony.

Structure of Reacted Antimony Oxide/Alumina and Silica Catalysts. The Sb 3d_{3/2} XPS binding energy for Sb₂O₅ is 539.7-540.5 eV [40]. The Sb 3d_{3/2} XPS binding energy measured for Sb₂O₃ is 539.5 eV. Thus, since the binding energy difference between Sb³⁺ and Sb⁵⁺ is approximately 0.7 eV, XPS cannot readily distinguish between these two species [41-44]. Since the difference in binding energies is small, a broad peak results when both peaks are present. Thus, curve fitting of the Sb XPS peak has some ambiguity. As a result, it is not possible to determine if changes are occurring as a function of reaction condition.

Comparison of Antimony Oxide on Alumina and Silica. The concentration of the surface OH groups/surface area of the alumina support is 1.7×10^{-3} mmol/m² and for the

silica support the value is 9.1×10^{-4} mmol/m² [45]. Thus, the ratio of hydroxyls of the alumina support to the hydroxyls of the silica is approximately 2:1. If it is assumed that one Sb-alkoxide reacts with one hydroxyl on the support, monolayer capacity of the alumina is expected to be approximately 35 wt.% and of silica approximately 40 wt.% (taking the surface area of the support into effect). XPS and XRD data for the alumina and silica supported catalysts are in agreement with this prediction.

Influence of Catalyst Structure on CO Oxidation Activity. CO oxidation reactions have shown that the most active catalysts contain 10 to 20 wt.% loadings of Sb₂O₅. As the loading increases (> 25 wt.%) in both series, the activity of the catalyst decreased. In the case of 30–40 wt.% Sb/Al₂O₃ the activity is lower than that of the support. As for SiO₂, the activity decreases to approximately 0.8% which is higher than that of the pure support (0.4%). The drastic change in the support from that of the 40 wt.% catalyst may be due to the activity of Sb₂O₅ itself. This is shown by the activity of the higher loadings of the active phase. At the loadings of greatest activity, it is possible that a spillover, as seen with Pt catalysts, is occurring between the Sb and the support. The trend of observing a maximum then as the loading increases lends support to this explanation. Once the surface approaches saturation with the Sb phase, the interaction sites available between the support and the Sb decrease, which decreases the activity of the catalyst itself. Davydov [46] used CO to probe V₂O₅/Al₂O₃ catalysts and observed spillover of carbon-oxygen species from the active vanadium pentoxide component on the alumina carrier.

CO oxidation on the aluminum antimonate support showed an increase in conversion over the supported Sb₂O₅/Al₂O₃. This suggests that the interaction between Sb and Al is important in this reaction. Straguzzi et al. [10] studied CO oxidation and found that at 460°C the conversions were less than 10% and showed activity of 1.0 mmol/m²h. Straguzzi suggests that because of the difficulty in reducing Al³⁺, the activity of the aluminum antimonate is attributed to Sb cations.

4.5. Conclusions

The use of surface and bulk spectroscopic techniques and CO oxidation activity data for $\text{Sb}_2\text{O}_5/\text{Al}_2\text{O}_3$ and $\text{Sb}_2\text{O}_5/\text{SiO}_2$ catalysts leads to the following conclusions:

1. XRD and XPS data indicate that Sb is well dispersed over the Al_2O_3 and SiO_2 carriers.
2. Semi-quantitative XRD for Al_2O_3 suggests that less than 0.2 wt.% crystallites of Sb_2O_5 are present and less than 0.5 wt.% crystallites of Sb_2O_5 are present in the SiO_2 supported catalysts. We tentatively ascribe this to errors in catalyst preparation.
3. The binding energy of Sb indicates that the antimony is in the +5 oxidation state in both catalysts and is independent of Sb loading and reaction conditions.
4. CO oxidation suggests that the highest activity occurs with active phase loadings of 10-20 wt.% Sb_2O_5 on both Al_2O_3 and SiO_2 . As loading increases above this level, the activity decreases. This is tentatively ascribed to spillover.

References

1. R.K. Grasselli and J.D. Burrington, *Adv. Catal.*, **30**, 133, 1981.
2. R.K. Grasselli, *React. Kinet. Catal. Lett.*, **35**, 327, 1981.
3. G. Centi and F. Trifirò, *Catal. Rev. Sci. Eng.*, **28**, 165, 1986.
4. J.C. Vedrine, G. Coudurier, M. Forissier, and J.C. Volta, *Catal. Today*, **1**, 261, 1987.
5. F.J. Berry, *Adv. Catal.*, **30**, 97, 1981.
6. S.E. Golunski and D. Jackson, *Appl. Catal.*, **48**, 123, 1989.
7. R.K. Grasselli and J.L. Callahan, *J. Catal.*, **25**, 273, 1972.
8. G.I. Straguzzi, K.B. Bischoff, T.A. Koch, and G.C. Schuit, *Appl. Catal.*, **25**, 257, 1986.
9. G.I. Straguzzi, K.B. Bischoff, T.A. Koch, and G.C. Schuit, *J. Catal.*, **103**, 357, 1987.
10. G.I. Straguzzi, K.B. Bischoff, T.A. Koch, and G.C.A. Schuit, *J. Catal.*, **104**, 47, 1987.
11. F. Sala and F. Trifirò, *J. Catal.*, **34**, 68, 1974.
12. V. Fattore, Z.A. Furhman, G. Manara, and B. Notari, *J. Catal.*, **37**, 223, 1975.

13. M. Burriesci, F. Garbassi, M. Petrisa, and G. Petrini, *J. Chem. Soc., Faraday Trans. 1*, **78**, 817, 1982.
14. I. Aso, S. Furukawa, N. Yamazoe, and T. Seiyama, *J. Catal.*, **64**, 29, 1980.
15. Y. Boudeville, F. Figueras, M. Foissier, J-L. Portefaix, and J.C. Vedrine, *J. Catal.*, **58**, 52, 1979.
16. J.L. Barclay, J.R. Bethell, J.B. Bream, D.J. Hadley, R.H. Jenkins, D.G. Stewart, and B. Wood, Brit. Patent 864,666.
17. F.J. Berry and D.J. Smith, *J. Catal.*, **88**, 107, 1984.
18. J.C. Volta, B. Benaichouba, I. Mutin, and J.C. Vedrine, *Appl. Catal.*, **8**, 237, 1983.
19. G.A. Zenkovets, D.V. Tarasova, T.V. Andrushkevich, G.I. Aleshina, T.A. Nikoro, and R.G. Ravilov, *Kinet. Catal.*, **20**, 380, 1979.
20. M.-Y. Lo, S.K. Agarwal, and G. Marcelin, *J. Catal.*, **112**, 168, 1988.
21. I.L. Mikhailova, I.S. Sazonova, N.P. Keier, and T.V. Belodtseva, *Kinet. Katal.*, **9**(3), 565, 1968.
22. F.M. Ali-Zade, N.M. Mardanova, P.M. Sorgin, R.M. Talshinskii, A.A. Medzhidov, and R.G. Rizaev, U.S.S.R. Patent 49,052,169, 1991.
23. S. Blumrich, R. Brand, B. Engler, W. Honnen, and E. Koberstein, European Patent 410,440, 1991.
24. Y. Ohno and K. Morishita, Japanese Patent 49,052,169, 1974.
25. G. Busa, *Langmuir*, **2**, 577, 1986.
26. G.C. Bond, S. Flamerz, and R. Shukri, *Faraday Discuss. Chem. Soc.*, **87**, 65, 1989.
27. Y. Gushikem, C.R.M. Peixoto and L.T. Kubota, *New Developments in Ion Exchange, ICIE*, 607, 1991.
28. S. Denofre, Y. Gushikem, and C.U. Davanzo, *Eur. J. Solid State Inorg. Chem.*, **28**, 1295, 1991.
29. M. Shirai, K. Asakura, and Y. Iwasawa, *J. Phys. Chem.*, **95**, 499, 1991.
30. G.C. Bond and K. Brückman, *Faraday Discuss. Chem. Soc.*, **72**, 235, 1981.
31. E.C. Alyea, K.F. Brown, and K.J. Fisher, *J. Mol. Catal.*, **63**, L11, 1990.
32. E.V. Benvenutti, Y. Gushikem, C.U. Dananzo, S.C. de Castro, and I.L. Torriani, *J. Chem. Soc. Faraday Trans.*, **88**, 3193, 1992.
33. A. Proctor, University of Pittsburgh.
34. C. Defosse, P. Canesson, P. G. Rouxlet, and B. Delmon, *J. Catal.*, **51**, 269, 1979.
35. F. P. J. M. Kerkhof and J. A. Moulijn, *J. Phys. Chem.*, **83**, 1612, 1979.
36. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 129, 1979.
37. D. R. Penn, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 29, 1976.
38. E.V. Benvenutti, Y. Gushikem, C.U. Dananzo, S.C. de Castro, and I.L. Torriani, *J. Chem. Soc. Faraday Trans.*, **88**, 3193, 1992.
39. A. Li-Dun, J. Zhi-Cheng, and Y. Yuan-Gen, in "Catalyst Deactivation 1987", ed. B. Delmon and G.F. Froment, 159, 1987.
40. R.A. Lemberanskii, F.M. Poladov, I.B. Annenkova, and A.P. Shepelin, *React. Kinet. Catal. Lett.*, **32**(1), 103, 1986.
41. W.E. Morgan, W.J. Stec, and J.R. Van Wazer, *Inorg. Chem.*, **12**, 953, 1973.

- 42. T. Birchall, J.A. Connor, and I.H. Hiller, *J. Chem. Soc., Dalton Trans.*, 2003, 1975.
- 43. A.F. Orchard and G. Thornton, *J. Chem. Soc., Dalton Trans.*, 1238, 1977.
- 44. F. Garbassi, *Surf. Interface Anal.*, **2**, 165, 1980.
- 45. J. Kijenski, A. Baiker, M. Glinski, P. Dollenmeier, and A. Wokaun, *J. Catal.*, **101**, 1, 1986.
- 46. A.A. Davydov, *Zh. Fiz. Khim.*, **65**, 1803, 1991.

Chapter 5

Future Work

5.1. Characterization

Characterization of Mixed Metal Oxide Catalysts. In addition to the use of XPS to determine the nature and distribution of the active sites in complex mixed oxides, ion scattering spectroscopy (ISS) can also provide information on the active sites(s) following various reactions. In the case of vanadium oxide and antimony oxide monolayer catalysts, reactions of the surface phase with the reducing molecules could lead to surface migration and subsequent multilayer formation. Monolayer-to-multilayer transitions can be difficult to follow using XPS due to the relatively large sampling depth of the technique. Thus, ISS can be useful to follow subtle changes in the geometry of the vanadium oxide and antimony oxide caused by surface reactions. Along with XPS, Raman spectroscopy can also provide information on the active site(s) under various reaction conditions. Raman spectroscopy can also be used to monitor differences in the chemical reactivity of surface species present.

In addition to using EPR to identify V^{4+} in the reacted vanadium oxide on aluminum antimonate catalysts, it would also be useful to characterize the active site(s) by performing *in situ* reaction studies on both the $V/AlSbO_4$ and Sb/SiO_2 and Sb/Al_2O_3 systems. An example of this use of EPR can be found by the double bond isomerization of butene over γ -alumina [1]. Both the isomerization reactions and the butene-deuterium exchange reaction have been extensively studied with a view to understanding the nature of the active sites on alumina.

NMR can also be used in much the same way as EPR to study active site(s), by using ^{13}C NMR studies of adsorbed molecules. For example, Stejskal et al. [2] studied

physically adsorbed CO_2 on zeolites. In addition, ^{13}C NMR has been used to study chemisorbed molecules [3]. NMR is unique in its ability to view molecules on the time scale of a surface reaction. Since the motion of molecules and ions on the surface is an integral part of heterogeneous catalysis, these studies have aided in the development of a dynamic picture of adsorption and proton mobility.

In situ IR will also provide information on the adsorption of probe molecules or reaction gases on the active site(s) of the catalysts. The IR cell shown in Figure 5.1 will allow the catalyst to be studied under controlled atmosphere and temperature. The gases can be delivered to the *in situ* IR cell by the system shown in Figure 5.2.

5.2. Vanadium Oxide/Aluminum Antimonate Catalysts

Propane Oxidation and Ammoxidation. As mentioned earlier, there has been an increased interest in selective oxidation and ammoxidation of inexpensive feedstocks, such as propane and methane. The next area of investigation would be the study of propane oxidation and ammoxidation over the V/AlSbO_4 catalyst. In order to learn more about the mechanism(s) for propane oxidation and ammoxidation, careful kinetics studies on the catalyst must be performed. In order to obtain this information, it will be necessary to study the effects of propane, oxygen and ammonia partial pressures on the rates of propylene, acrolein, acetaldehyde, acrylonitrile, acetonitrile and carbon oxides formation.

Centi et al. [4] reported that specific oxygen and ammonia concentrations exist which enhance the rates of propylene, acrylonitrile and acetonitrile formation over a V-Sb-W (1:5:1) Al_2O_3 (70 wt.%) catalysts. The kinetic experiments proposed will determine if there is a similar "optimum" ratio that exists for V/AlSbO_4 . If such a ratio exists, it will then be useful to perform IR and surface spectroscopic studies to determine the surface phases responsible for the enhanced catalytic properties.

Influence of Excess SbO_x on AlSbO_4 supported V catalysts. It is well known that

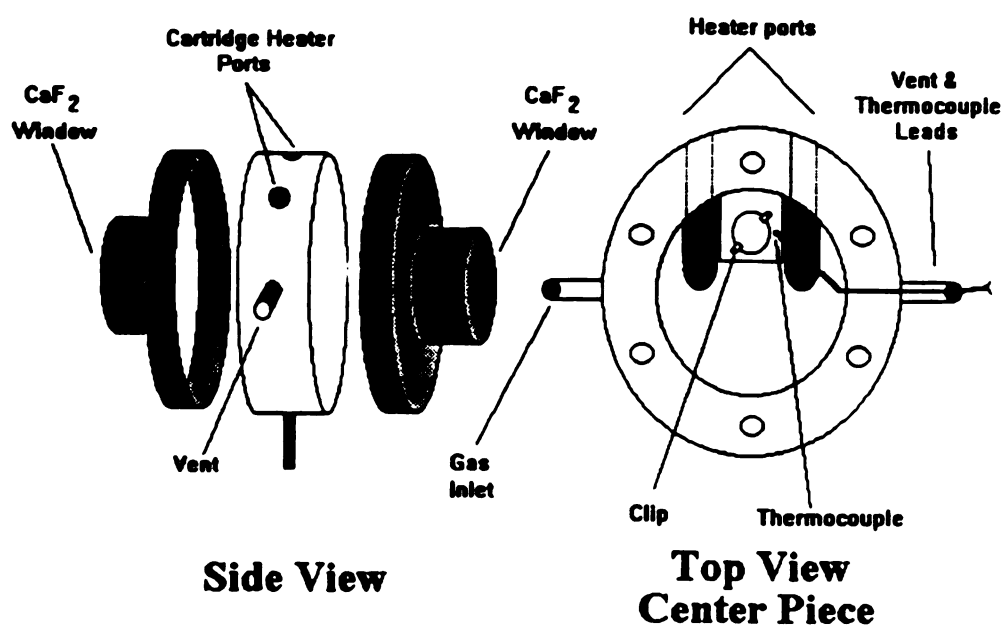


Figure 5.1. *In situ* IR cell.

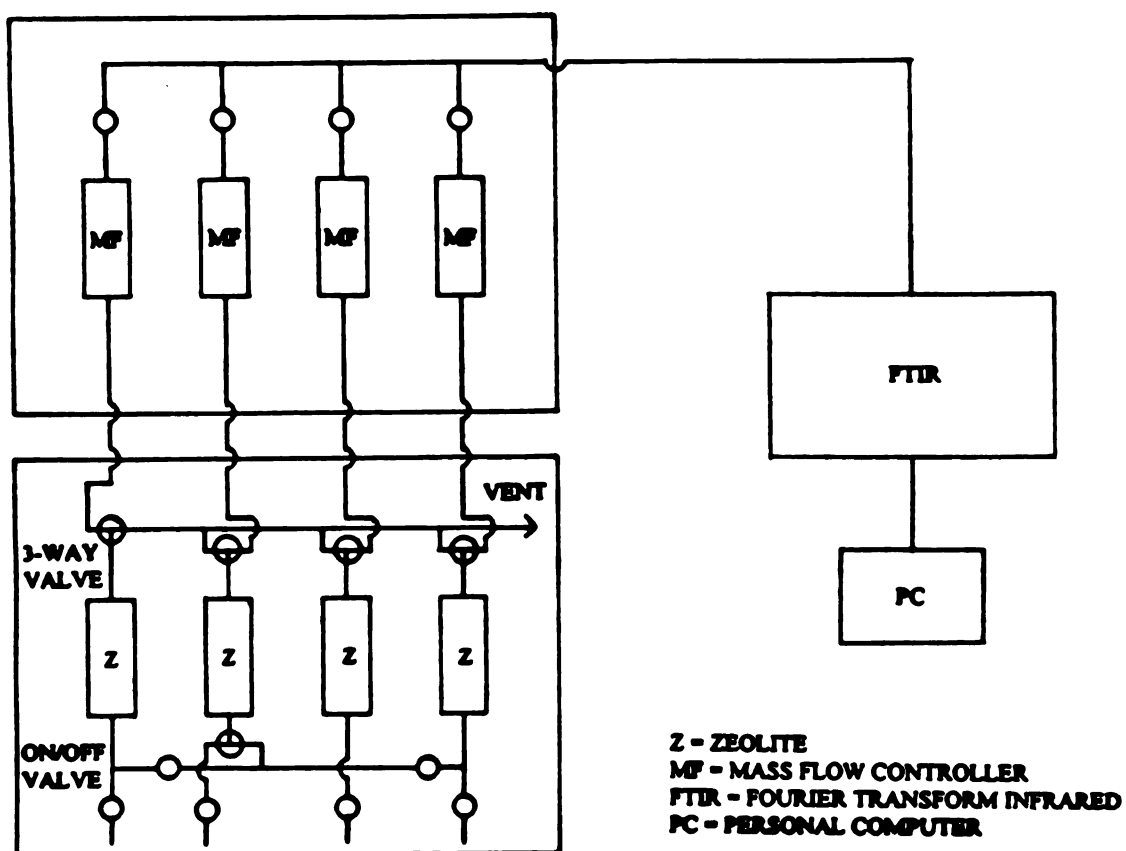


Figure 5.2. Gas handling system to *in situ* IR cell.

crystalline and monolayer phases have different effects on activity. Recently, Berry and Brett [5-7] reported that biphasic interactions between VSbO_4 and $\alpha\text{-Sb}_2\text{O}_4$ are important for the selective oxidation of propylene. However, the influence of excess SbO_x phase on the structure and activity of the catalysts is not well understood. The effects of excess SbO_x phase on the chemical state and dispersion of the supported V oxide and subsequently on the activity and selectivity of the mixed oxide catalysts for propylene and propane oxidation and ammoxidation should be investigated. From the different phases produced, it will be possible to determine the effects of crystalline SbO_x and highly dispersed SbO_x phases on the properties of V/AlSbO_4 catalyst. Future experiments will involve preparation and characterization of $\text{V/SbO}_x/\text{AlSbO}_4$ catalysts.

5.3. Antimony Oxide/ Supported Catalysts

Sb/Supported Catalysts. There has been considerable research effort in methane coupling and total oxidation of methane. As mentioned previously, Lo et al. [8] reported $\alpha\text{-Sb}_2\text{O}_4$ was a selective methane coupling catalyst. Dang and Ding [9] found that Sb/SiO_2 catalysts that contain an Sb-SiO_2 surface compound (Sb loadings < 5 %) are active for condensation reactions. However, the condensation activity decreases significantly on the formation of $\alpha\text{-Sb}_2\text{O}_4$ (Sb loadings > 5 %). Thus, the combination of methane coupling and condensation of isobutene and formaldehyde to isoprene may be useful reactions to probe the structure of supported Sb catalysts. It should be noted that regardless of the ability of the test reactions to probe the structure of the mixed oxides, valuable information about the nature of active site(s) in Sb supported catalysts will be obtained.

By varying the partial pressures of methane and oxygen it will be possible to study the effects of the partial pressures on the rate of carbon oxides produced. In addition, by having a higher level of methane it may be possible to control the selectivity of methane

coupling over total oxidation of methane. In order to increase the selectivity of total oxidation it would be necessary to have a higher partial pressure of oxygen over methane. However, these kinetic experiments will determine if optimum ratios exist for each reaction (i.e. methane coupling and total oxidation). If such a ratio exists, IR and surface spectroscopic studies will be used to determine the surface phases responsible for the enhanced catalytic properties.

In addition, the effect of calcination temperature on the catalyst structure and activity should be examined. Sb_2O_3 decomposes to form $\beta\text{-Sb}_2\text{O}_4$ at 730°C and $\alpha\text{-Sb}_2\text{O}_4$ at 950°C . By performing solid-state reactions, it will be possible to determine optimum conditions for methane coupling and/or total oxidation of methane as a function of antimony oxides formed.

5.4. Activation Energy

Activation Energy. It would also be useful to determine the activation energy for oxidation reactions of the V on aluminum antimonate and the Sb on alumina and silica, to improve our understanding of these reactions. Jonson et al. [10] have performed activation energy studies of V on titania. From this, it was found that at least two different active sites are present with a active phase loading of 0-0.5% V; one for the support, which is the least active phase and one for the vanadium species, which is the more active phase. Also, at 2% V and above, the active part of the support surface is covered and changes in the Arrhenius parameters can be attributed to the presence in these catalysts of an additional V species at higher loadings. By performing such activity measures and correlating the data with that obtained from spectroscopic techniques, it will be possible to better define the nature of metal oxide-support interaction and the influence of the metal oxide dispersion and reactivity on the catalytic properties of the mixed oxides.

References

1. J.H. Lunsford, L.W. Zingery, and M.P. Rosynek, *J. Catal.*, **38**, 179, 1975.
2. E.O. Stejskal, J. Schaefer, J.M.S. Henis, and M.K. Tripodi, *J. Chem. Phys.*, **61**, 2351, 1974.
3. J.J. Chang, A. Pines, J.J. Fripiat, and H.A. Resing, *Surface Sci.*, **47**, 661, 1975.
4. G. Centi, R.K. Grasselli, E. Patane, and F. Trifiro, "New Developments in Selective Oxidation," *Stud. Surf. Sci. Catal.*, **55**, 515, 1990.
5. F.J. Berry, M.E. Brett, and W.R. Patterson, *J. Chem. Soc. Dalton*, **1**, 9, 1983.
6. F.J. Berry, M.E. Brett, and W.R. Patterson, *J. Chem. Soc. Dalton*, **1**, 13, 1983.
7. F.J. Berry and M.E. Brett, *J. Catal.*, **88**, 232, 1984.
8. M.-Y. Lo, S.K. Agarwal, and G. Marcelin, *J. Catal.*, **112**, 168, 1988.
9. Z. Dang and S. Ding, *Fenzi Cuihua*, **1**(3), 146, 1987.
10. B. Jonson, B. Rebenstrol, R. Larsson, and S.L.T. Andersson, *J. Chem. Soc., Faraday Trans. 1*, **84**(10), 3547, 1988.