NTiS

STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES: PROGRESS REPORT, AUGUST 1, 1987-JULY 31, 1988

TEXAS UNIV. AT AUSTIN. DEPT. OF CHEMICAL ENGINEERING

JUL 1988
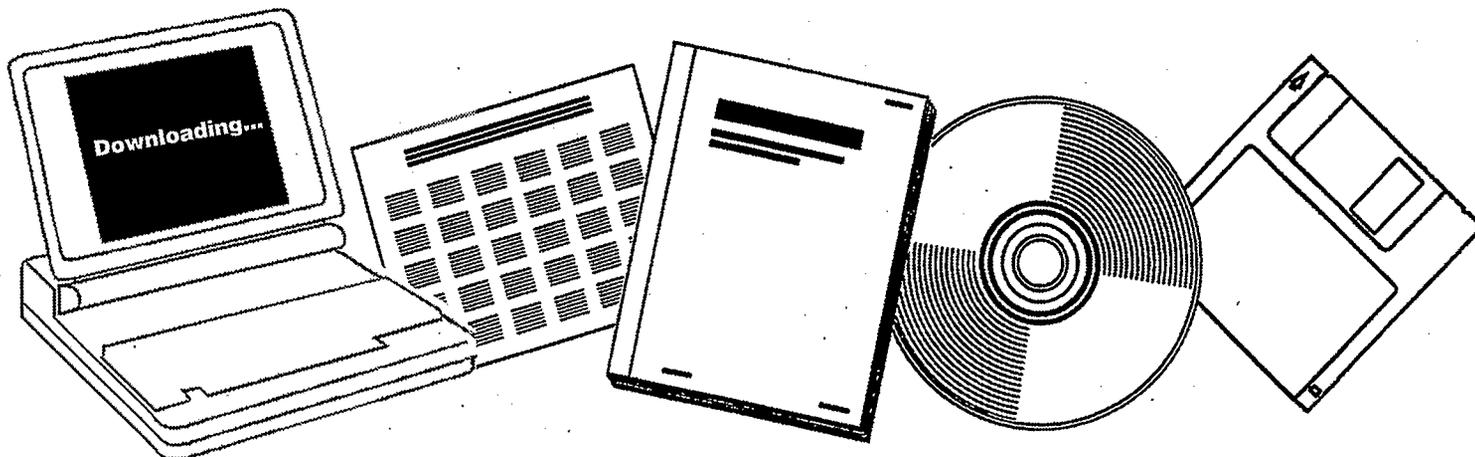
DOE/ER/13604--4

DE88 014731

STUDY OF SYNTHESIS GAS

CONVERSION OVER METAL OXIDES

Progress Report

August 1, 1987 - July 31, 1988

John G. Ekerdt

University of Texas
Austin, Texas 78712

July 1988

RESEARCH SCOPE AND OBJECTIVES

The goals of this program are to develop an understanding of the causes for catalytic activity and selectivity, and an understanding of the effects of metal oxide structure and acidic and basic additives on CO hydrogenation over metal oxides. The research has focused on synthesis gas conversion over zirconium dioxide to produce branched hydrocarbons and alcohols, isosynthesis. Reaction mechanisms have been identified by the use of infrared spectroscopy, transient reaction techniques, and carbon-13 and oxygen-18 isotope labelling. Isosynthesis is characterized by two competing growth steps, CO insertion and condensation between methoxide and enolates. Surface oxygen anion vacancies have been identified as the active site for CO activation by various adsorptive and reactive titrants.

Current work is focused on alkali hydroxide/, Al_2O_3/, Sc_2O_3/, Y_2O_3/ Sm_2O_3/ and La_2O_3/ZrO_2 systems. These systems were selected because acidity, basicity, oxygen anion vacancy concentration and oxide overlayer effects can be systematically altered. X-ray diffraction, XPS, BET, gravimetric uptake of CO and SO_3, and acid/base titration are used to characterize the catalysts. Conversion of CO to methanol, 2-alcohol dehydration, and labelling studies, which establish the relative rates of CO insertion versus condensation, are used to probe the catalytic properties of these systems.

DESCRIPTION OF THE RESEARCH EFFORT

During the past year we have focused on two issues: confirmation that anion vacancies are the active sites for CO activation and hydrogenation, and the influence of additives on the reactions that occur during isosynthesis. The anion vacancy study is completed and is discussed first. The influence of additives is ongoing and forms the basis for the work we will continue in

the next year.

The interaction of CO and CO/H_2 mixtures with ZrO_2 has been studied, and the species which formed and how they transformed are understood [1,2,3]. Our study was directed at establishing the role of the oxide surface in the activation of CO and in the formation of the C_1 fragments which are involved in methane and methanol formation at 1 atm [2] and in isosynthesis at 35 atm [4]. The active site for formate formation and reduction to methoxide had been suggested to be a surface anion vacancy [2]. Molecular probes were selected as the means to identify the site over ZrO_2. Carbon monoxide was expected to form a formate, CO/H_2 adsorption followed by hydrolysis of methoxide to methanol was expected to identify the methoxide surface concentration, and SO_3 was expected to react with anion vacancies and form a sulfate.

Sulfur trioxide was selected as an anion vacancy titrant for ZrO_2 on the basis of studies with SO_3 over other oxides and on the ability to form sulfate species over ZrO_2. Infrared studies over Fe_2O_3 by Yamaguchi et al. [5] showed that sulfur trioxide adsorbed as a sulfate species with a dioxo structure, $(FeO)_2S(=O)_2$. This was proposed to occur at oxygen anion vacancy sites. A sulfate species could also be formed over Fe_2O_3 from SO_2 in excess O_2 or by calcining $(NH_4)_2SO_4$ and $Fe(OH)_3$ [5]. A similar sulfate structure with dioxo ligands was proposed by Jin et al. [6] following calcination of $(NH_4)_2SO_4$ and $Zr(OH)_4$ at 600° C. A recent infrared study by Bensitel et al. [7] found that adsorption of H_2S or SO_2 in excess O_2 over ZrO_2 at 450° C resulted in the $(ZrO)_3S=O$ sulfate species. This same $(ZrO)_3S=O$ sulfate structure was also reported following impregnation of ZrO_2 with either H_2SO_4, $(NH_4)_2SO_4$ or $Zr(SO_4)_2$ followed by evacuation at 450° C [7].

The oxides of zirconium form three different phases, monoclinic, tetra-

gonal and cubic [8-10]. The monoclinic phase is stable below 1200° C. The tetragonal phase is normally stable above 1200° C, but can be obtained in a metastable condition at much lower temperatures and is the crystal structure of zirconia particles under 300 angstrom in diameter [11]. The cubic phase is formed at temperatures above 2280° C, but can be stabilized at room temperature by the addition of other oxides such as Y_2O_3 and CaO.

The uptake studies were performed over pure zirconia and over yttria-doped zirconia. It was not possible to make pure ZrO_2 which was all one phase and of sufficient area (at least 5 m^2 g^{-1}) for the gravimetric experiments. Only mixtures of monoclinic and tetragonal zirconia formed. Yttria doping of ZrO_2 was used to generate a single phase (cubic) and to introduce known concentrations of anion vacancies. This latter aspect results since stabilization of the cubic structure is accomplished by direct substitution of trivalent yttria cations for the host lattice Zr^{+4} cation. Since the dopant cation is of lower valence than the host cation, oxygen vacancies are created to preserve lattice neutrality. Spectroscopic studies have shown that the trivalent Y and tetravalent Zr cations are statistically distributed [12] and that the Zr cations are nearest neighbors to the anion vacancies [13]. These vacancies increase the electrical conductivity, with diffusing oxygen ions being the primary charge carrier [14-16]. This diffusion of oxygen ions has been associated with lattice vacancy migration [14,15].

A series of catalysts was prepared for this study. The composition and phases are presented in Table 1. The uptake results are presented in Table 2. Fourier-transform infrared spectroscopy was used to establish that CO adsorbed as a formate (as expected [3]). Therefore, the CO uptake results represent the amount of formate which adsorbed over the catalyst. The

TABLE 1

Catalyst Preparation and Characterization

Catalyst sample	Calcination temperature(°C)	Calcination time (hr)	BET surface area (m^2/g)	Mole% Y_2O_3	Phase [a] (M/T/C)
1	600	2	30.04	0.0	67/33/0
2	600	4	27.83	0.0	70/30/0
3	600	6	18.08	0.0	73/27/0
4	700	4	8.16	0.0	79/21/0
5	800	4	8.70	0.0	90/10/0
6	600	4	74.69	9.1	0/0/100
7	600	4	63.40	11.8	0/0/100
8	600	4	82.02	15.0	0/0/100
9	600	4	71.20	19.9	0/0/100
10	600	4	11.86	100.0	--------

a) Percent of monoclinic/tetragonal/cubic phases present in the catalyst.

TABLE 2

Gravimetric Uptake and Titration Results

Catalyst sample	Mole% Y_2O_3	Molecules SO_3 adsorbed/m^2 (x 10^{-17})	Molecules CO adsorbed/m^2 (x 10^{-17})	Molecules CH_3OH titrated/m^2 (x 10^{-17})
1	0.0	17.1	3.09	7.16
2	0.0	28.5	6.00	5.72
3	0.0	43.5	11.1	7.93
4	0.0	20.5	16.2	16.2
5	0.0	35.2	18.2	12.2
6	9.1	11.9	3.06	2.64
7	11.8	6.25	1.02	2.14
8	15.0	3.94	0.94	0.28
9	19.9	6.74	1.50	0.20
10	100.0	8.73	6.02	0.08

methanol titration methods were developed in earlier studies in our group [1,2] and the results reported in Table 2 were similar. This similarity suggests that methanol titration represents the formate which was hydrogenated to methoxide. Infrared spectroscopy was used to establish that SO_3 adsorbed as the $(ZrO)_3S-O$ sulfate species. Repeated dose experiments were performed in which SO_3 was adsorbed and desorbed six or seven times in different atmospheres to establish that sulfate formation was reversible and that SO_3 was not reacting with surface hydroxyl groups or adsorbed oxygen atoms.

There are two critical issues associated with SO_3: the structure of the adsorbed species and whether or not SO_3 reacts with anion vacancy sites during adsorption. The IR studies were used to assign the structure the $(ZrO)_3S-O$ sulfate species by comparison to the work of Bensitel et al. [7]. It is not possible to use the uptake results over the monoclinic/tetragonal mixtures to determine if the sulfate formed at anion vacancy sites because a constant phase composition could not be generated. Yttria doping of ZrO_2 was used to generate a single phase (cubic) and to introduce known concentrations of anion vacancies. By assuming the surface and bulk Y_2O_3 concentration and the associated anion vacancies to be equal it was possible to calculate the theoretical number of anion vacancies. The uptake results in Table 2 were divided by the predicted values (for the (100) plane) to give the results listed in Figure 1. The 9.1% Y_2O_3 stabilized ZrO_2 (YSZ) had the highest uptake for all probes. The theoretical uptake for SO_3 was exceeded over 9.1% YSZ. Arguments [17] were presented to explain the results presented in Figure 1. These arguments considered the effect of Y_2O_3 on the probe molecules and the materials properties of doped zirconia. Vacancy mobility is
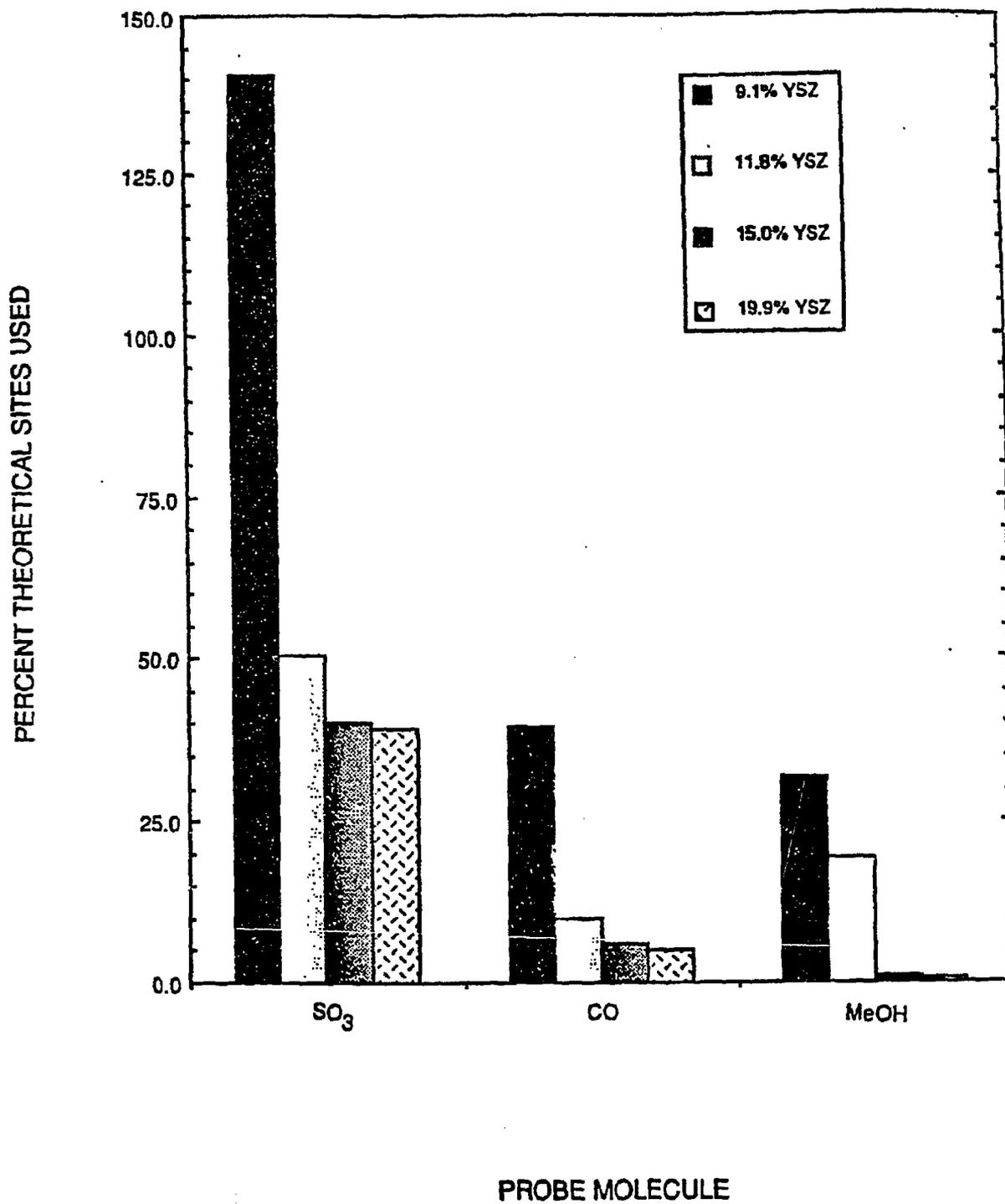
Figure 1. Percent of the Teoretical Sites Used by the Various Probe Molecules.

highest in the 9.1% YSZ sample and significantly depressed in the other YSZ samples. We reasoned that SO_3 reacted with the vacancies; because of their mobility in the 9.1% sample the vacancies could migrate to the surface. We proposed that the uptake studies over YSZ confirm that SO_3 reacted with anion vacancies.

Methanol was produced in a noncatalytic reaction to determine the number of methoxide species which formed. Methanol can be produced in a catalytic reaction over ZrO_2 at atmospheric pressure [2,18] and over both ZrO_2 and yttria stabilized ZrO_2 at 35 atm [4]. Methoxide is the precursor to methanol [2]. Sulfur trioxide adsorbed at anion vacancy sites. The SO_3 uptake data and methanol titration data (Table 2) for catalyst samples 1-9 are plotted in Figure 2. With the exception of the datum point corresponding to catalyst sample 4, which was reproduced several times for SO_3 and methanol, there is a reasonable correlation between the amount of methanol formed and the amount of SO_3 adsorbed as sulfate. Catalyst samples which contained different amounts of monoclinic, tetragonal and cubic zirconia are represented in Figure 2. Similar correlations (not shown) were found when the amount of CO adsorbed as formate was plotted versus the amount of SO_3 adsorbed or when CO adsorbed was plotted versus methanol formed. These correlations support the proposal made earlier [2] that CO hydrogenation to methanol proceeds over anion vacancy sites.

Figure 3 presents the mechanism for CO interaction with ZrO_2, which was presented in an earlier publication [2], and a representation of SO_3 reacting with a vacancy site on the ZrO_2 surface. Hydroxyl groups are not shown in Figure 3A because our studies did not indicate any role of hydroxyl groups in sulfate formation. (Hydroxyl groups were present during all of the experi-
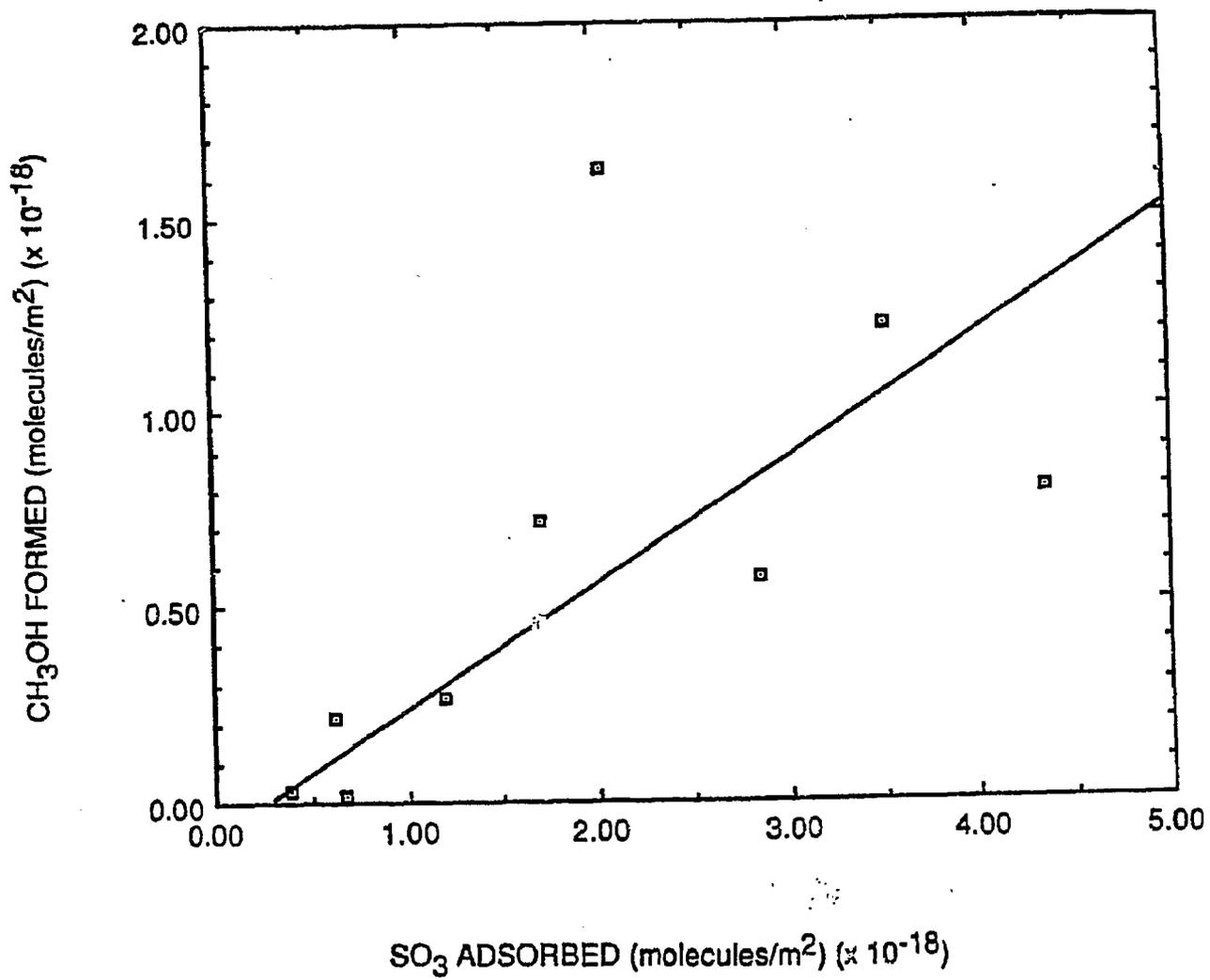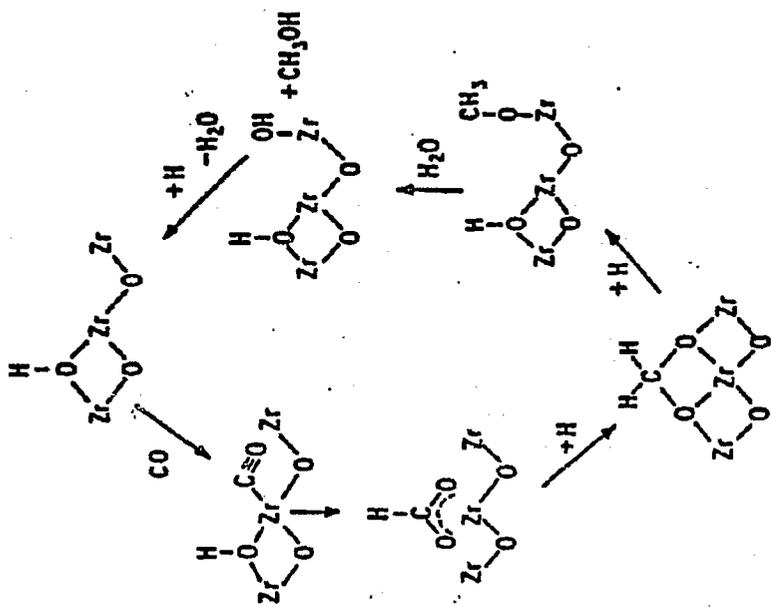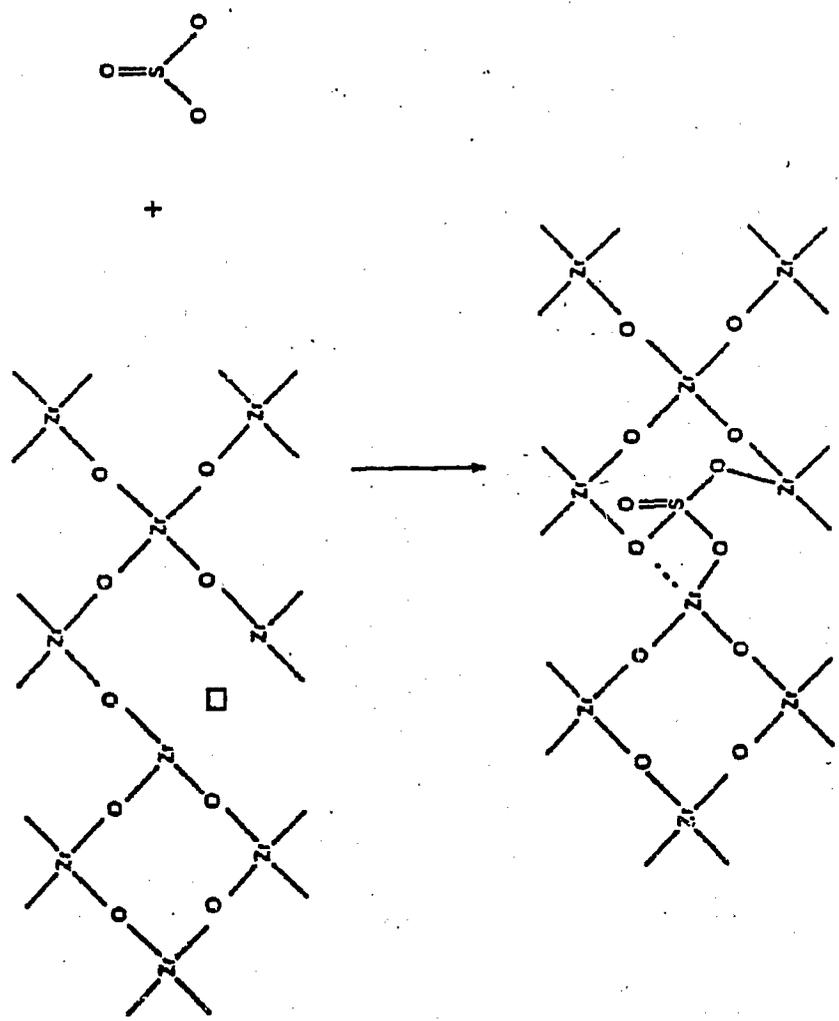
Figure 2. Molecules of Methanol Formed versus the Molecules of SO_3 Adsorbed.

Figure 3. Proposed Scheme for the Interaction of the Probe Molecules with ZrO₂

ments.) Desorption in argon or oxygen, during the repeated dose experiments, should have prevented repopulation of hydroxyl groups. If hydroxyl groups play a role in the uptake of SO_3, this would have led to a continuous decrease in SO_3 uptake with continued dosing/desorption cycles. Bensitel et al. [7] also did not find any infrared evidence for hydroxyl interaction with SO_2 during sulfate formation.

The chemistry for hydrocarbon synthesis over ZrO_2 was investigated and reported [2,4]. The reactions which lead to higher weight products are presented in Figures 4 and 5. We have been interested in establishing the surface characteristics of metal oxides which give rise to and influence the reactions presented in these figures. Our approach has been to investigate how acid and base additives and vacancy concentration influence the relative rates of CO insertion and condensation. We have prepared a variety of doped zirconias and have examined the effect of dopant type and concentration on the selectivity at 35 atm and 425° C to identify trends with dopant level. These catalysts have been analyzed by X-ray diffraction and XPS. Figures 6 and 7 are representative of the activity and selectivity patterns with vacancy level (Figure 6) and basicity (Figure 7). Causes for these trends can be established through the use of carbon-13 labeled acetone and propion-aldehyde which will permit us to determine, in an absolute manner, the effect of additives on the rates of CO insertion and condensation for linear and branched propagating species. Carbon labelling was used to establish the mechanisms [4]. We will also investigate secondary alcohol dehydration selectivity to 1- and 2-olefins because the key intermediate in dehydration, an enolate, is also a key intermediate (VIII and X) in the CO hydrogenation mechanisms shown in Figures 4 and 5. Nothing definitive can be stated at the
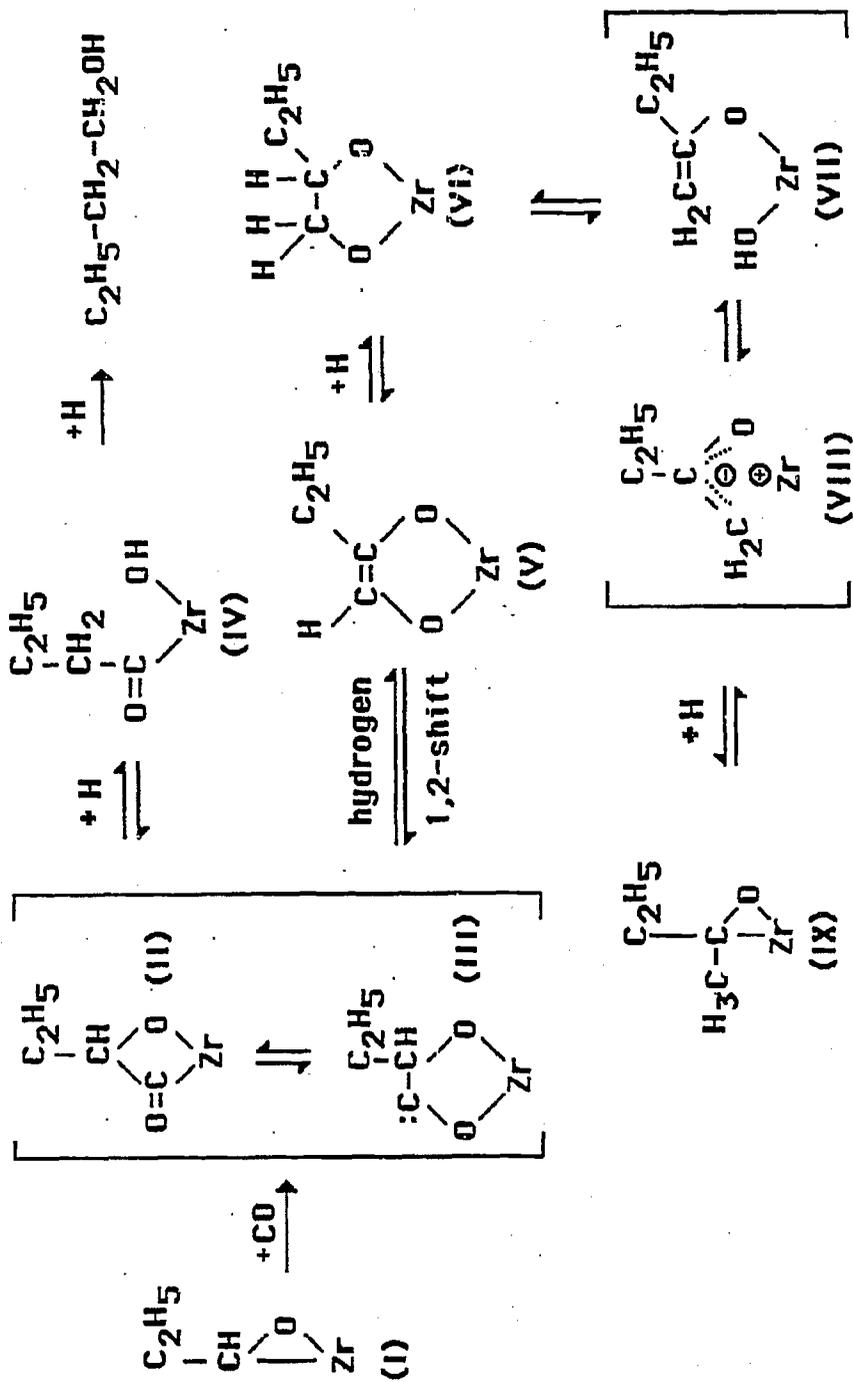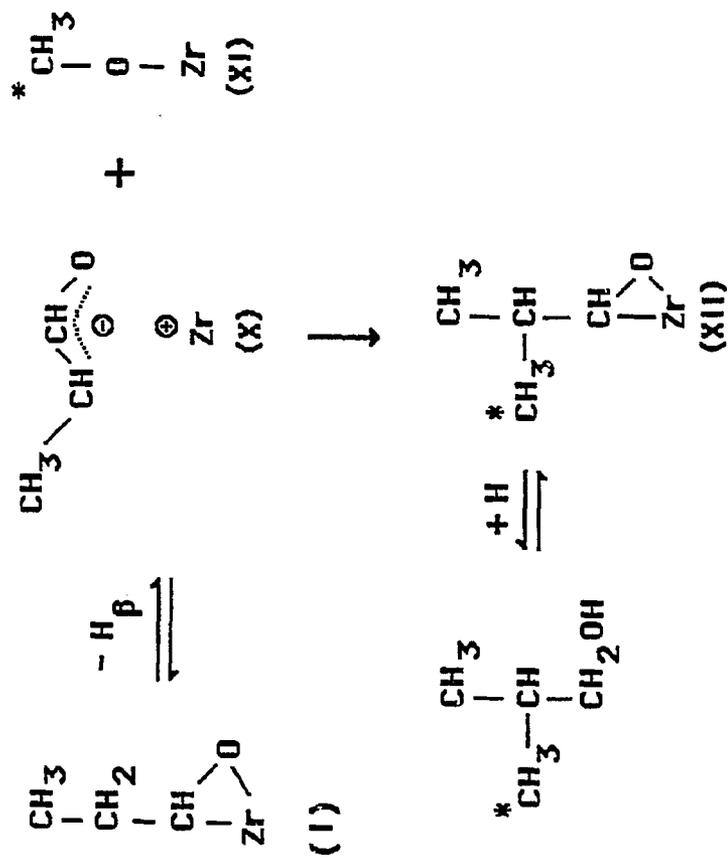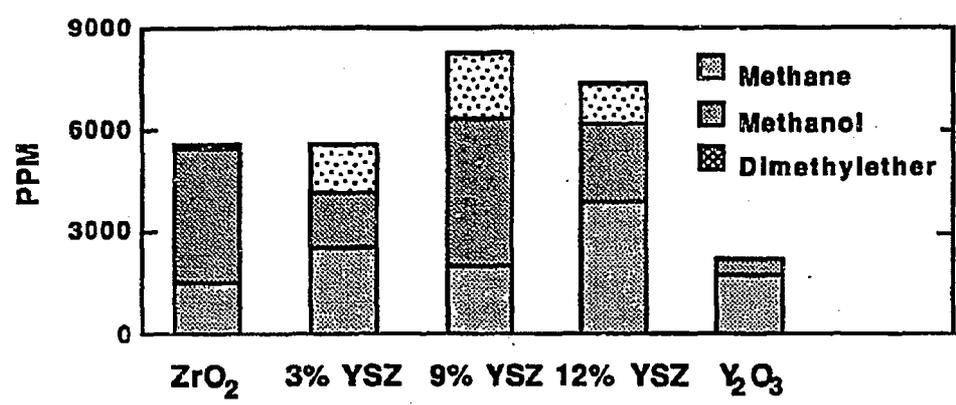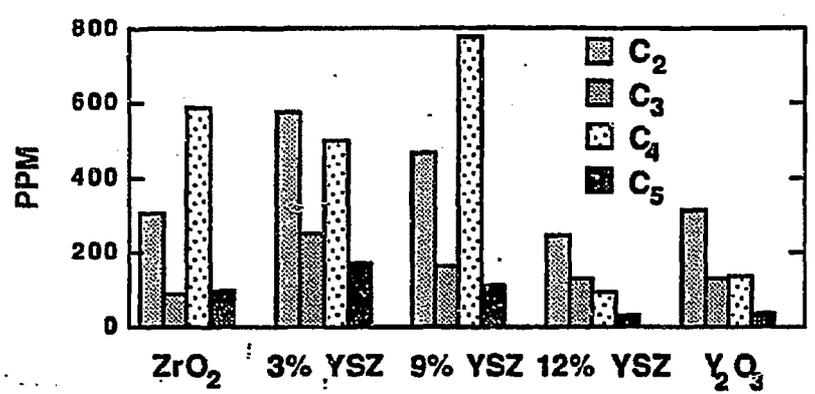
Figure 4. CO Insertion Reaction

$*CH_3 - O - Zr$ (XI)

$+$

$CH_3 \diagdown CH \diagup CH \diagdown O$
$\ominus$
Zr $\oplus$ (X)

$\longrightarrow$

CH_3
$|$
$CH - CH \diagdown O$
$|$ Zr
$*CH_3$ (XII)

$- H_\beta$

$+ H$

$CH_3 - CH_2 - CH \diagdown O$
Zr
(I)

CH_3
$|$
$*CH_3 - CH - CH_2OH$

Figure 5.   Condensation Reaction

Products from Methoxide Species

Alkane and Olefin Production over Zirconia/Yttria Catalysts

Branched-to-Linear Ratio for
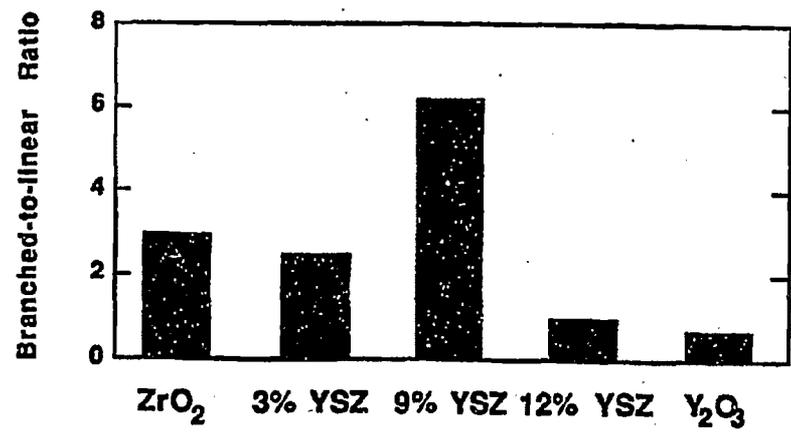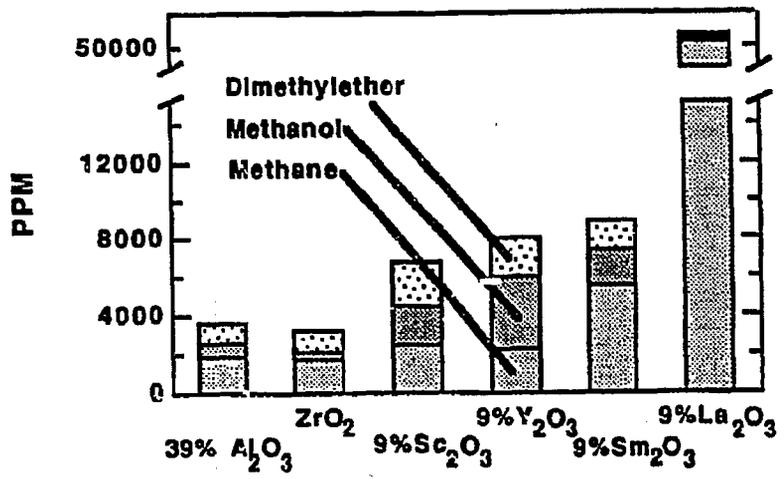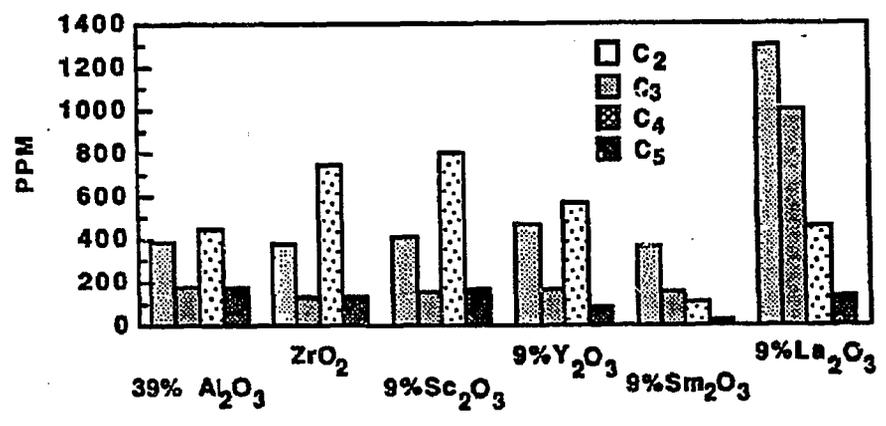## Alkanes and Olefins over Zirconia/Yttria Catalysts

Figure 6. Product Distribution over Yttria Stablized Zirconias

Products from Methoxide Species from Zirconia-Mixed Metal Oxide Catalysts

Alkane and Olefin Production over Zirconia-Mixed Metal Oxide Catalysts

Branched-to-Linear Ratios for Zirconia-Mixed Metal Oxide Catalysts
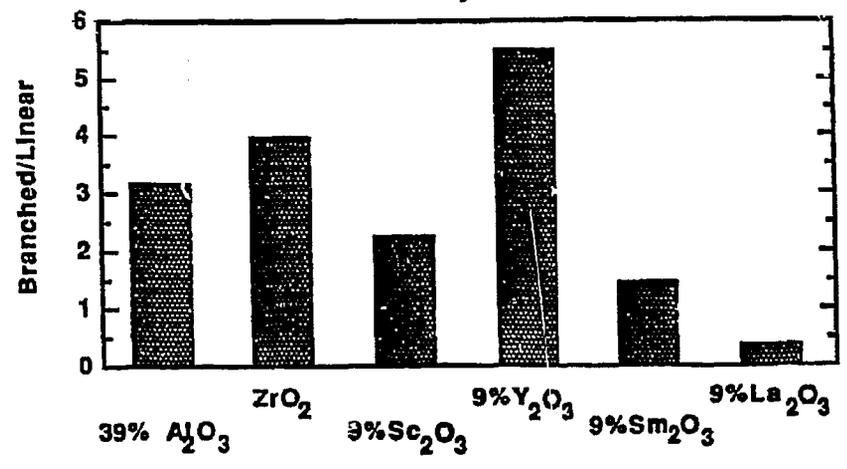

Figure 7. Product Distribution over Yttria Stablized Zirconias

present about the chemistry of these doped oxides. The experimental approach
we will used to understand this catalytic chemistry is presented below.

FUTURE RESEARCH

To understand the surface characteristics that cause a metal oxide to
have the unique selectivity of the isosynthesis reaction we will investigate
the effect of oxygen anion vacancies, oxygen mobility, acid and base
strength, alkali promoters and pretreatment effects. The objective will be
met by examining isosynthesis selectivity changes, alcohol dehydration selec-
tivity changes and the relative rates of CO insertion and condensation reac-
tions over specifically formulated catalysts.

Oxygen Anion Vacancies. The effect of oxygen anion vacancies will be
investigated by synthesizing YSZ at 3, 7, 9 and 12 percent yttria. The
addition of each Y cation to ZrO_2 creates half an anion vacancy. Figure 6
clearly shows methoxide activity, isosynthesis activity and isosynthesis
selectivity are at a maximum where vacancy mobility is at a maximum and where
SO_3 also showed a maximum. The effect of increasing methoxide surface con-
centrations should be revealed with this system.

Oxygen Mobility. In small percentages of stabilizer addition, the anion
vacancies appear to be arranged at random throughout the lattice structure.
Above 9-10% stabilization with Y_2O_3 the anion vacancies are believed to form
domains causing the mobility (and ionic conductivity) to decrease signifi-
cantly [19-21]. This change from random to ordered vacancies occurs at a
percentage unique to each stabilizer. The role of oxygen mobility will be
investigated by studying the four YSZ's plus three catalysts stabilized with
calcia at 13, 15, and 17% calcia. These mixtures are chosen because ZrO_2 is
not fully stabilized below 12-13% CaO. The maximum conductivity of CSZ is at

13% and decreases at higher stabilization [14].

Acid/Base Effect. Several metal oxides of varying acid/base strength will be added to ZrO_2 to ascertain the effect on the isosynthesis reaction. Oxides will be mixed with ZrO_2 at 9%. Listed in order of increasing basicity these include: $Sc_2O_3 < Y_2O_3 < Sm_2O_3 < La_2O_3 < CaO$. The ionic radius of the cations increase with basicity to the point where La^{+3} is thought to be too large to fit into a cubic fluorite structure. Therefore, it gives rise to a perchlorite structure and anion vacancies are ordered leading to less ionic conductivity. This "ordering" of vacancies may not effect the number of vacancies on the surface, but it does lower the oxygen mobility [14].

Alumina has also been incorporated into the acid/base study because the "best" isosynthesis catalyst was identified to be 39% Al_2O_3/ThO_2 [22,23].

Alkali Promoters. Alkali promoters added as alkali hydroxides, have been reported to enhance higher alcohol formation over Cu/ZnO catalysts. This is thought to occur because the large alkali cations stabilize the enolate intermediate in the condensation reaction. The more basic the promoter, the larger the alkali cation, the better it was found to promote higher alcohol formation [24]. Four alkali hydroxide solutions will be added to the ZrO_2 catalyst to measure the effect of the promoter and the relative effect of the basicity/cation size of the promoter.

Isosynthesis Reaction. The effect of these catalysts have on the isosynthesis reaction will be investigated by studying the conversion, branched-to-linear ratio and the product distribution. Product distribution will include whether or not is it the characteristic isosynthesis distribution (ZrO_2 in Figures 6 and 7) and what is the C_1 product distribution. Since branched products form by both propagation reactions (Figures 4 and 5), ^{13}C-

labelled acetone and propionaldehyde will be used to differentiate the rates of these two propagation reactions. The effects on enolate stabilization will be investigated with the 2-alcohol dehydration selectivity.

REFERENCES

1. He, M-Y., and Ekerdt, J. G., J. Catal. 90, 17 (1984).

2. Jackson, N. B., and Ekerdt, J. G., J. Catal. 101, (1986).

3. He, M-Y, and Ekerdt, J. G., J. Catal. 87, 381 (1984).

4. Tseng, S. C., Jackson, N. J., and Ekerdt, J. G., J. Catal. 109, 284 (1988).

5. Yamaguchi, T., Jin, T., and Tanabe, K., J. Phys. Chem. 90, 3148 (1986).

6. Jin, T., Yamaguchi, T., and Tanabe, K., J. Phys. Chem. 90, 4794 (1986).

7. Bensitel, M., Saur, O., Lavalley, J-C., and Morrow, B. A., Mater. Chem. Phys. 19, 147 (1988).

8. McCullough, J. D., and Trueblood, K. N., Acta Cryst. 12, 507 (1959).

9. Evans, P. A., Stevens, R., and Binner, J. G. P., Trans. J. Brit. Ceram. Soc. 83, 39 (1984).

10. Scott, H. G., J. Mater. Sci. 10, 1527 (1975).

11. Garvie, R. C., J. Phys. Chem. 69, 1238 (1965).

12. Dexpert-Ghys, J., Faucher, M., and Caro, P., J. Solid State Chem. 84, 179 (1984).

13. Catlow, C. R. A., Chadwick, A. V., Greaves, G. N., and Moroney, L. M., J. Amer. Ceram. Soc. 69, 272 (1986).

14. Etsell, T. H., and Flengas, S. N., Chem. Rev. 70, 339 (1970).

15. Heyne, L., in "Mass Transport in Oxides", National Bureau of Standards Special Publication 296, 149 (1968).

16. Kingerly, W. D., Pappis, J., Doty, M. E., and Hill, D. C., J. Amer.

Ceram. Soc. 42, 393 (1959).

17. Silver, R. G., and Ekerdt, J. G., "The Role of Lattice Anion Vacancies in the Activation of CO and as the Catalytic Site for Methanol Synthesis over Zirconium Dioxide," Submitted to J. Catal.

18. Abe, H., Maruya, K-I., Domen, K., and Onishi, T., Chem. Lett. Chem. Soc. Japan, 1875 (1984).

19. Butler, C. V., Catlow, C. R. A., and Fender, B. E. F., Radiation Effects 73, 273 (1983).

20. Catlow, C. R. A., Solid State Ionics 12, 67 (1984).

21. Mackrodt, K. W. C., and Woodrow, P. M., J. Amer. Ceram. Soc. 69, 277 (1986).

22. Pichler, H., and Ziesecke, K-H., Brennst. Chem. 30, 360 (1950).

23. Pichler, H., and Ziesecke, K-H., Bur. Mines Bull. 448 (1950).

24. Yamaguchi, T., Nakano, Y., and Tanabe, K., Bull. Chem. Soc. Japan 51, 2482 (1978).