STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES: PROGRESS REPORT, AUGUST 1, 1988-JANUARY 31, 1989

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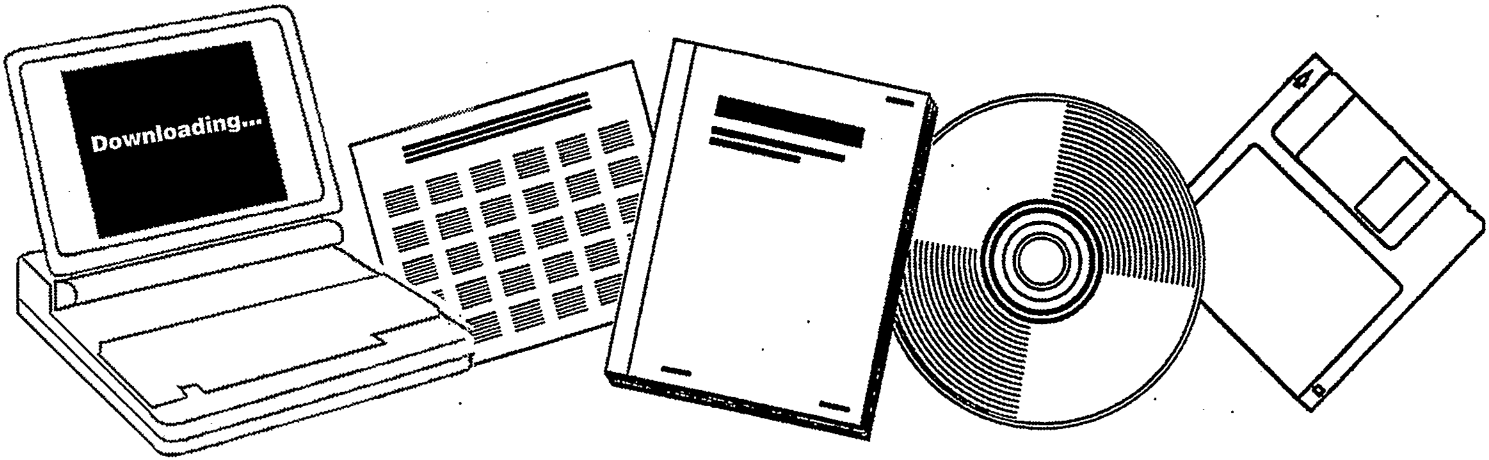

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STUDY OF SYNTHESIS GAS CONVERSION OVER METAL OXIDES

Progress Report

August 1, 1988 - January 31, 1989

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January 1989

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RESEARCH SCOPE AND OBJECTIVES

The goals of our 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 program has concentrated on zirconium dioxide systems and has: (1) identified the structure of adsorbed C_1 fragments [1-3], (2) used oxygen isotopes to establish the reaction mechanisms for methanol and methane synthesis from synthesis gas [3,4], (3) used ^{13}C-labelled reactants to establish the complex reaction mechanisms (CO insertion into adsorbed aldehydes and condensation between methoxide and η^3-enolates) by which higher molecular weight hydrocarbons and alcohols are formed [5], (4) identified lattice oxygen vacancies as the active site for CO adsorption and conversion into methoxide as well as the site for C_1 synthesis [6], and (5) investigated the role of basic and acidic surface sites in stabilizing key intermediates in the synthesis of higher weight products.

The research has focused on synthesis gas conversion over oxides which are selective to branched hydrocarbons and alcohols. The reaction is referred to as isosynthesis. Our work in this area involved research at one and 35 atm. The strategy was first to determine the reaction mechanisms responsible for isosynthesis and second to determine how the catalyst structure and composition stabilized key intermediates in the isosynthesis reaction and thereby influenced the selectivity to the branched hydrocarbons and alcohols. The mechanisms have been identified and we are nearing completion of the study of how zirconia activates CO and why zirconia is inherently selective to branched hydrocarbons and alcohols.

Current work is focused in two areas: (1) on alkali hydroxide, Al_2O_3,

Sc_2O_3, Y_2O_3, Sm_2O_3, La_2O_3, and CaO supported on ZrO_2 and (2) on the synthesis, characterization and catalytic activity of oxide overlayers formed from monometallic and bimetallic dinuclear organometallic complexes. The latter forms the basis for the renewal proposal. The former will be completed under the current grant and is the focus of this report. Zirconium catalyzed systems were selected because acidity, basicity, and oxygen anion vacancy concentrations can be systematically altered and their influence on CO hydrogenation catalysis explored. X-ray diffraction, XPS, BET, gravimetric uptake of CO and SO_3, and temperature programmed desorption 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 zirconia systems.

DESCRIPTION OF THE RESEARCH EFFORT

The zirconium catalysts are prepared by precipitation from a solution of the chloride salts at high pH to form a mixed hydroxyl gel which is then calcined to give a high area (5-60 m^2/g) oxide. Concentration of the additive, such as Y_2O_3, is changed in a systematic manner by changing the ratio of Zr and Y in the salt solution. Additives have been selected which should give surface Zr/additive ratios that are similar to the bulk composition. The actual ratio was checked with XPS and found to be close to the bulk composition.

Figure 1 presents our proposed scheme for the activation of CO and the synthesis of C_1 products [4]. Carbon monoxide was proposed to adsorb at anion vacancy sites as a formate and transform into a methoxide via oxymethylene or formaldehyde. The methoxide and formaldehyde intermediates are

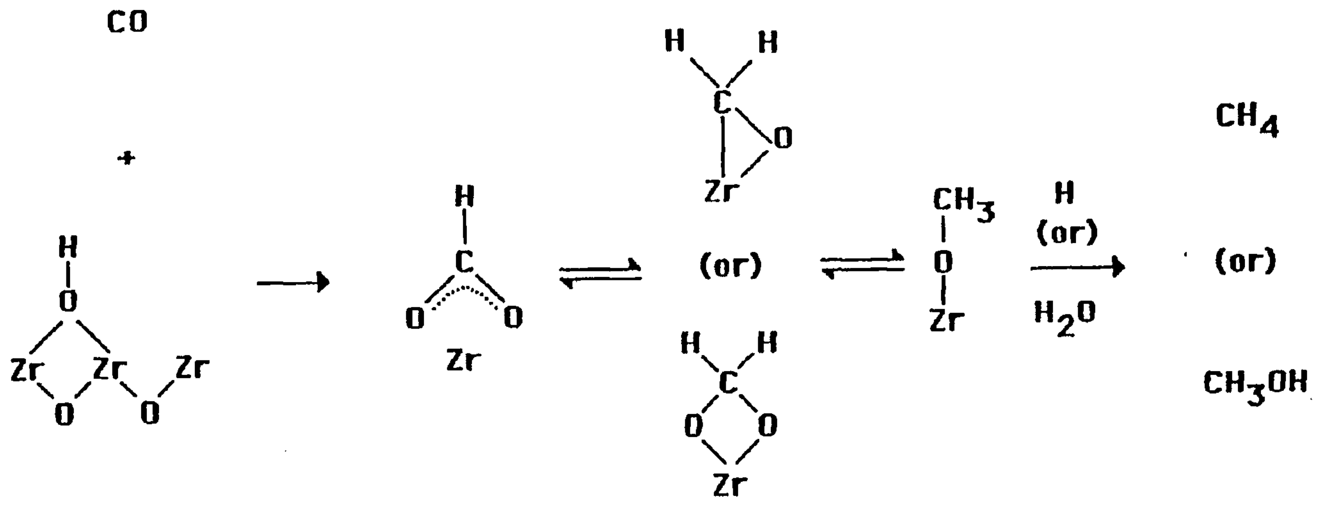CO
+
H
O
Zr
Zr
Zr
O
O
H
C
O
O
Zr
H
H
C
O
Zr
(or)
H
H
C
O
O
Zr
CH3
O
Zr
H
(or)
H2O
CH4
(or)
CH3OH

FIGURE 1

also involved in the synthesis of higher weight products. The proposed reactions for isosynthesis are presented in Figures 2 and 3 and were established through the use of ^{13}C-labelled reactants [5] during the grant period. The primary chain growth step involves CO insertion into a bound aldehyde or ketone. An aldehyde (I) is shown in Figure 2 leading to the formation of both linear and branched C_4 products. The CO insertion reaction would be initiated with the formaldehyde intermediate shown in Figure 1. The second chain growth step, and the one that is likely responsible for extensive branching in the hydrocarbon products, involves a condensation reaction between methoxide and an η^3-enolate (X in Figure 3). Selective titrants were used to determine if the anion vacancy sites shown in Figure 1 are the sites at which CO adsorbs and is converted into the key C_1 intermediates for higher chain growth. Acidic and basic additives were incorporated into the zirconia to understand how zirconia functions in the reactions shown in Figures 2 and 3.

Site Determination We proposed to use SO_3 as a probe of anion vacancy sites. Sulfur trioxide was selected as a potential titrant for anion vacancies because Yamaguchi et al. [7] had suggested that SO_3 reacted at anion vacancy sites over Fe_2O_3 to form a dioxo sulfate, $(FeO)_2S(=O)_2$ and because sulfate structures had been reported over ZrO_2 when other sources of sulfur were employed [8,9]. The experimental approach [6] involved four molecular probes, SO_3 adsorption, CO adsorption, CH_3OH titration and steady-state catalytic synthesis of CH_3OH and CH_4; each selected because it tested different aspects of the mechanism shown in Figure 2. The probes were used over a series of ZrO_2 catalysts that were subjected to different extent of calcination, and over a series of yttria doped ZrO_2 catalysts (see Table 1).

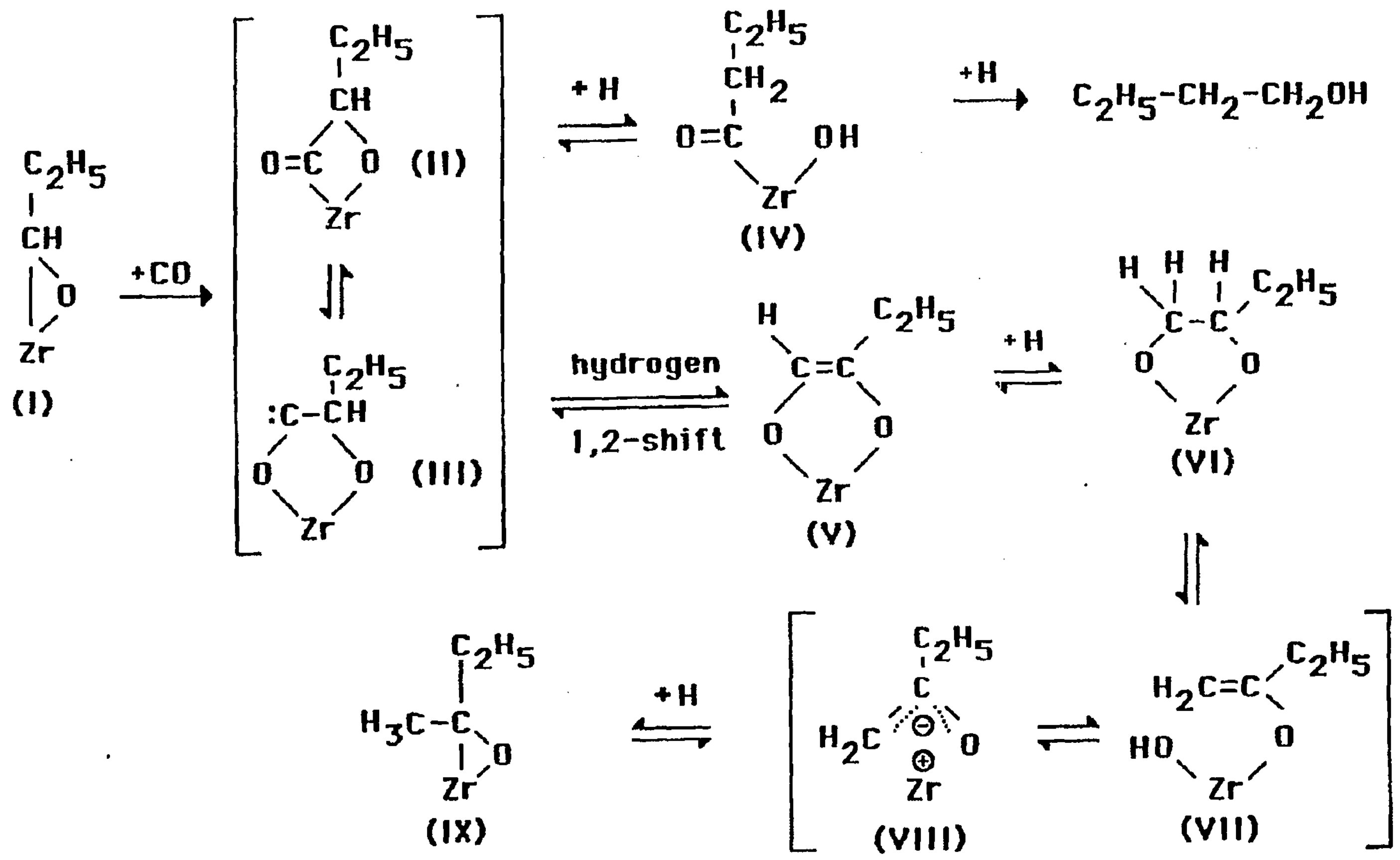
(I)
+CO
(II)
(III)
+H
(IV)
+H
$C_2H_5-CH_2-CH_2OH$
hydrogen
1,2-shift
(V)
+H
(VI)
(VII)
(VIII)
+H
(IX)

FIGURE 2

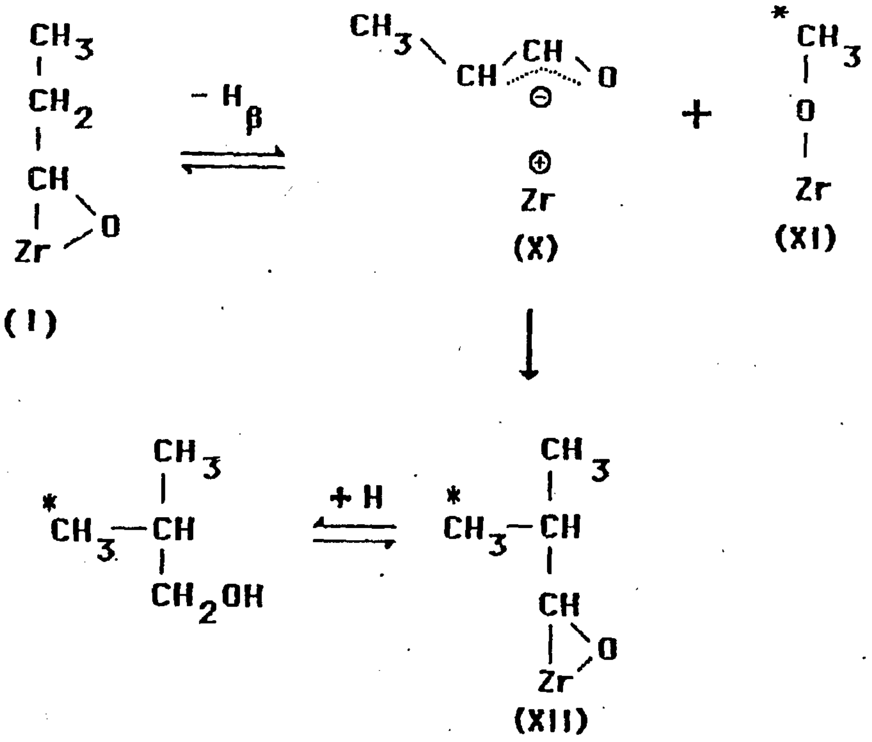

FIGURE 3

TABLE 1

Catalyst Preparation and Composition

Catalyst sample	Calcination temperature(°C)	Calcination time(hr)	BET surface area(m^2/g)	Composition[(a)] (Zr/Y)	Phase[(b)] (M/T/C)
1	600	2[(c)]	30.04	100.0/ 0.0	67/33/0
2	600	4	27.83	100.0/ 0.0	70/30/0
3	600	6	18.08	100.0/ 0.0	73/27/0
4	700	4	8.16	100.0/ 0.0	79/21/0
5	800	4	8.70	100.0/ 0.0	90/10/0
6	900	5	10.18	100.0/ 0.0	100/ 0/0
7	600	4	59.33	96.7/ 3.3	0/90/10
8	600	4	61.72	95.0/ 5.0	0/56/44
9	600	4	73.80	93.0/ 7.0	0/20/80
9'	900	5	29.50	93.0/ 7.0	0/15/85
10	600	4	74.69	90.9/ 9.1	0/ 0/100
15	600	4	96.44	90.2/ 9.8	0/ 0/100
15'	900	5	30.94	90.2/ 9.8	0/ 0/100
11	600	4	63.40	88.2/ 11.8	0/ 0/100
11'	900	5	21.95	88.2/ 11.8	0/ 0/100
12	600	4	82.02	85.0/ 15.0	0/ 0/100
13	600	4	71.20	80.1/ 19.9	0/ 0/100
14	600	4	11.86	0.0/100.0	-

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a) Mole percent ZrO_2 and Y_2O_3 present.

b) Percent of monoclinic, tetragonal and cubic phases present.

c) Removed from the oven immediately after calcination and cooled to 25 °C.

We initiated the titration studies over pure ZrO_2 catalysts. We explored the effect of calcination time and temperature, quench time after calcination, pretreatment in O_2 and then H_2 versus just O_2, and source of ZrO_2 (nitrate solution, chloride salt, isopropoxide complex) on the amount of SO_3 and CO adsorbed. The amount of SO_3 and CO adsorbed changed in parallel. It was not possible to associate adsorption with anion vacancies because the pure ZrO_2 samples consisted of a mixture of monoclinic and tetragonal phases which changed with thermal treatment. Yttria doped ZrO_2 was used in this study because each molecule of Y_2O_3 introduced into the lattice introduces an anion vacancy. It was felt that we could adjust the relative level of anion vacancies by changing the dopant level. We used XPS to establish that there was no significant surface segregation of yttria; the bulk and surface compositions were similar and showed no anomalous differences with loading level.

The catalysts listed in Table 1: were all prepared from the chloride salts, were pretreated in O_2 and then H_2 at 600 °C, and were removed from the calcining furnace immediately after calcination. As expected [10] calcination of ZrO_2 caused sintering and altered the amount of monoclinic and tetragonal ZrO_2. TEM studies revealed that as the calcination time was increased at 600 °C (samples 1, 2 and 3) or as the temperature was increased (samples 2, 4, 5 and 6, and samples 9, 9', 11, 11', 15 and 15') the particle morphology changed; the bonding between the particles changed from point contact to surface sharing and the individual particle shape changed from irregular to more or less equiaxed.

Table 2 summarizes the adsorption/titration/reaction results. Infrared spectroscopy was used to determine that SO_3 adsorbed at 110 °C as the

TABLE 2

Gravimetric Uptake and Titration Results

Catalyst sample	Molecules SO_3 adsorbed/m^2 ($x10^{-17}$)	Molecules CO adsorbed/m^2 ($x10^{-17}$)	Molecules CH_3OH titrated/m^2 ($x10^{-17}$)	C_1 rate molecules/m^2-sec ($x10^{-12}$)
1	17.1	3.09	7.04	22.48
2	28.5	6.00	6.61	17.08
3	43.5	11.1	7.68	27.72
4	20.5	16.2	14.1	79.67
5	35.2	18.2	10.9	92.50
6	40.6	19.2	8.23	32.58
7	1.57	1.10	0.89	3.50
8	3.13	1.52	1.15	4.22
9	4.98	1.88	2.08	4.75
9′	11.47	4.68	4.18	9.54
10	11.9	3.06	2.64	7.43
15	9.73	3.23	2.86	7.02
15′	25.9	8.83	6.27	21.91
11	6.25	1.02	2.14	5.55
11′	15.69	5.11	5.34	-
12	3.94	0.94	0.28	2.82
13	6.74	1.50	0.20	5.17
14	8.73	6.02	0.008	14.38

$(ZrO)_3S{=}O$ sulfate over ZrO_2. Infrared and temperature programmed desorption were used to confirm that CO adsorbed as formate over ZrO_2 and yttria doped ZrO_2. Through control experiments it was possible to show that methanol titration provided a relative measure of the amount of methoxide present over both ZrO_2 and yttria doped ZrO_2. The C_1 synthesis results provide a measure of the catalytic activity. Figure 4 plots the results over the yttria doped zirconias which were calcined for 4 hr at 600 °C (excludes samples 9', 11' and 15'). Figure 5 presents the amount of methanol titrated versus the amount of SO_3 adsorbed for all but catalyst sample 14 (pure yttria). Figure 6 presents the results over the yttria doped zirconias which were calcined at both 600 and 900 °C (samples 9, 9', 11, 11', 15 and 15'). It is possible to show that the probe molecules did not interact exclusively with surface yttrium cations but rather interacted with ZrO_2 modified by yttria. All of the probe molecules are seen in Figure 4 to have a maximum for the 9.1% or 9.8% yttria doped ZrO_2 catalysts (catalyst samples 10 and 15). Pure Y_2O_3 had a higher uptake of SO_3 and CO than the 11.8, 15.0 and 19.9% catalysts (Table 1). A high surface yttrium cation concentration may explain why the uptake of SO_3 and CO increased for catalyst 13, which had the highest yttria loading, 19.9%, compared to catalyst 12 (15% Y_2O_3). We proposed [6] that the maximum uptake over the 9.1% sample was associated with the mobility of anion vacancies. (Catalyst samples 9', 11', 15 and 15' were not included in Reference 6.) These vacancies are most mobile in the 9.1% catalyst (see below) and are possibly drawn to the surface because the vacancy can undergo reaction with the probe molecules. We also proposed that a correlation between anion vacancy mobility and SO_3 uptake supports the hypothesis that SO_3 interacts with anion vacancies.

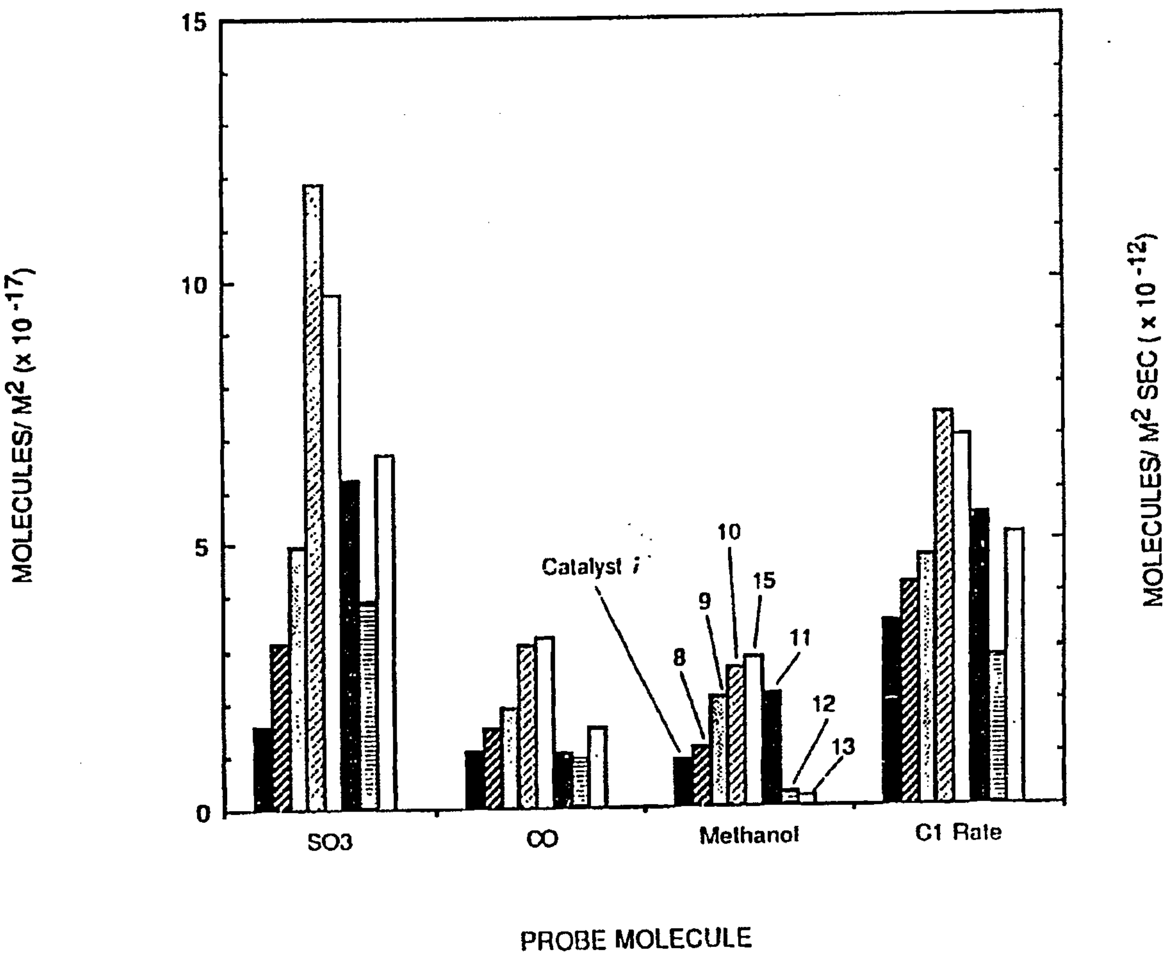

15
10
5
0
MOLECULES/ M^2 (x 10^{-17})
MOLECULES/ M^2 SEC (x 10^{-12})
Catalyst i
8
9
10
15
11
12
13
SO3
CO
Methanol
C1 Rate
PROBE MOLECULE

FIGURE 4

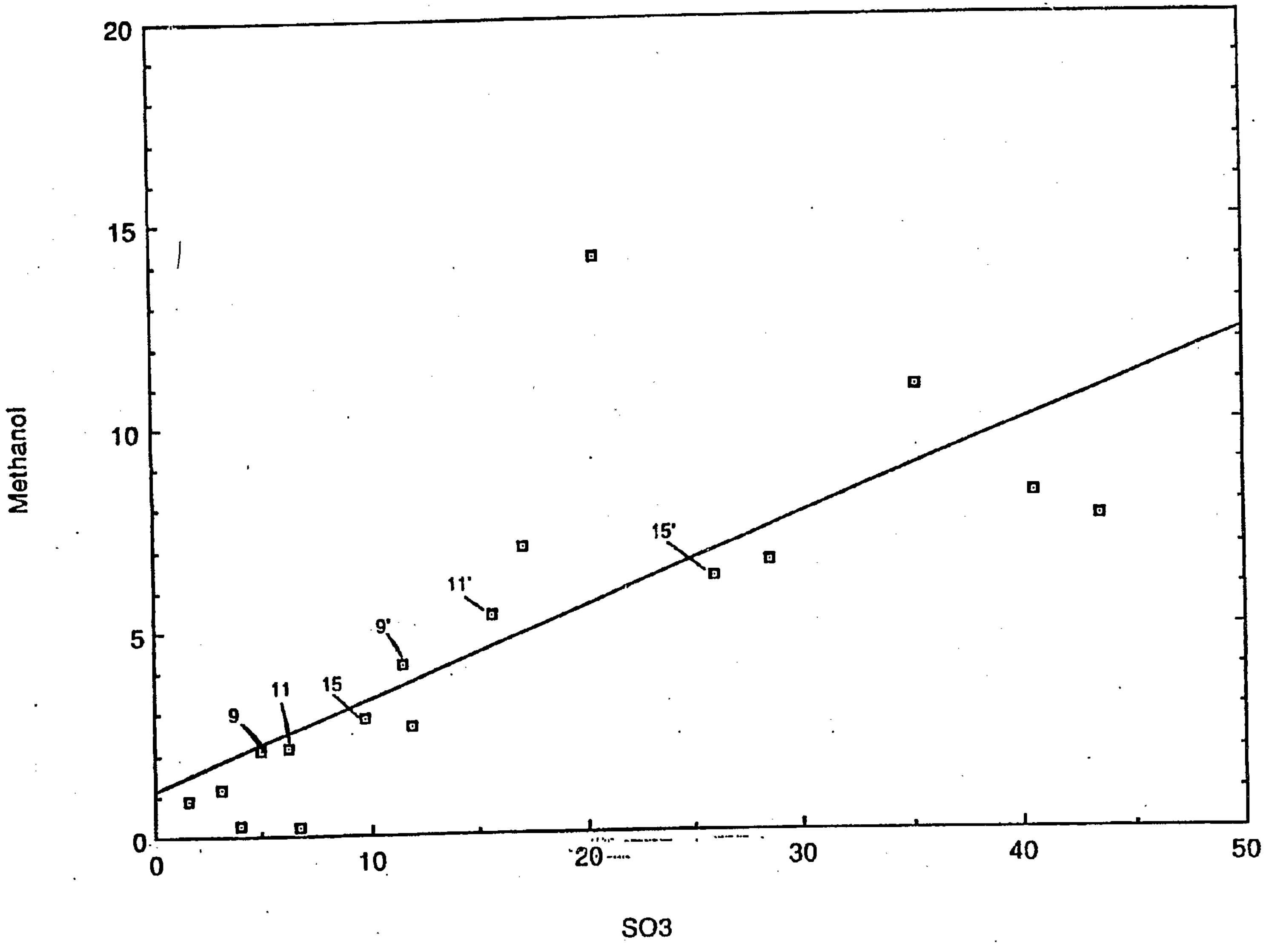
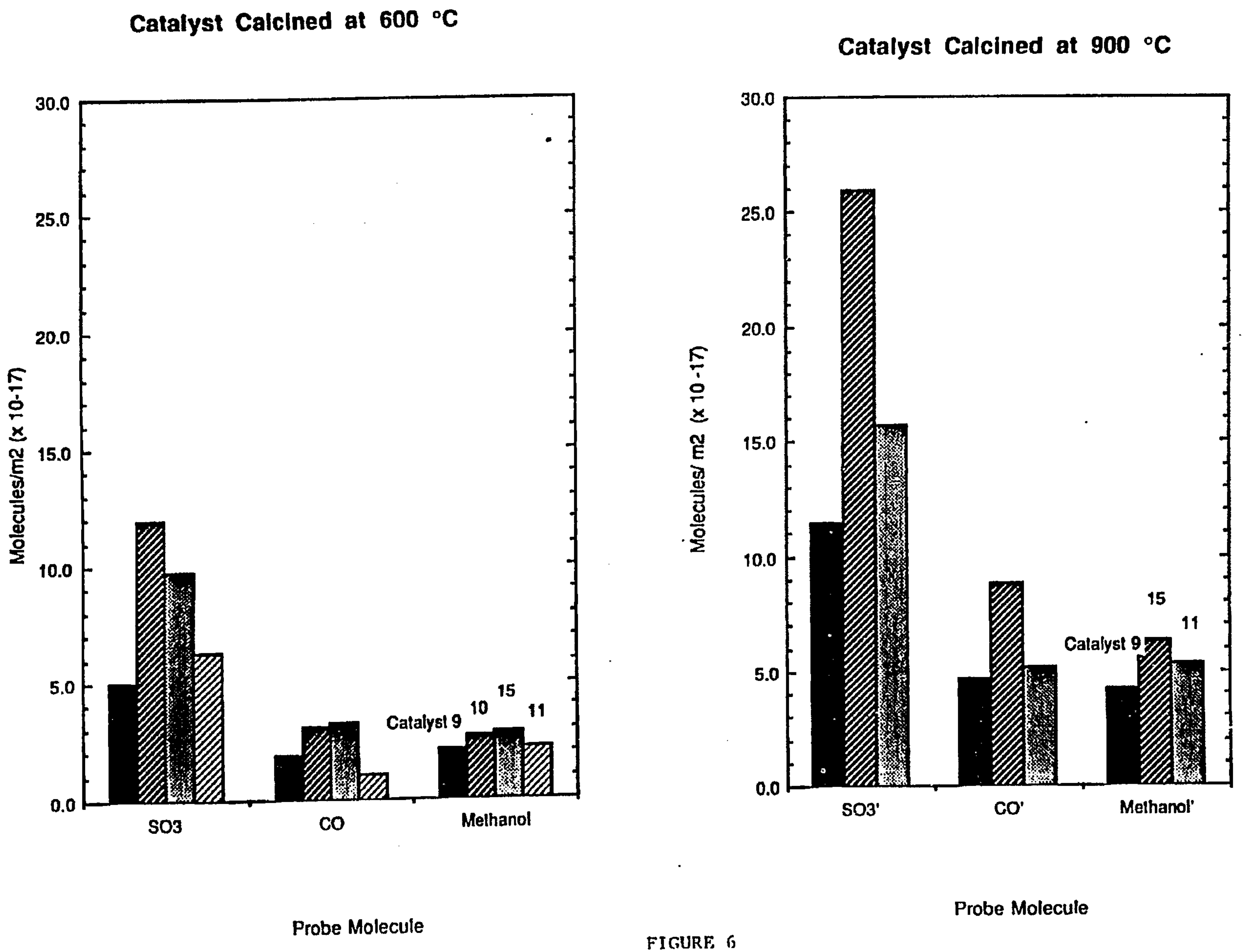


FIGURE 5


Catalyst Calcined at 600 °C

Catalyst Calcined at 900 °C

FIGURE 6

Yttria doped zirconias (and pure ZrO_2) are electrically conductive. The conductivity is ionic and proceeds by vacancy migration. In general, for stabilized zirconia, the conductivity has a maximum somewhat above the lowest doping level that is required to make the cubic structure [11]. Six to eight mole percent yttria is required to stabilize ZrO_2 fully and the conductivity maximum appears around 10% [12,13]. This could explain why 9.1% (and 9.8%) Y_2O_3 had the greatest interaction with the probe molecules. The conductivity at 15% Y_2O_3 is an order of magnitude less than the maximum value. The decrease in conductivity with increasing dopant ion concentration has been associated with dopant-vacancy interactions, vacancy-vacancy interactions or the formation of microdomains [13]. Decreasing conductivity means that vacancy migration is reduced and vacancies would be less able to migrate to the surface and undergo the reactions proposed above.

Figure 5 shows that a correlation exists between the amount of methanol formed and the amount of SO_3 adsorbed as sulfate. Similar correlations can be found by using other combinations of data from Table 2. Each of these probes involve a different surface process with the proposed active site. No one chemical or physical property of ZrO_2 could be systematically changed without simultaneously changing other properties. Correlations showing increasing methanol formation, CO adsorption or C_1 synthesis with increasing SO_3 uptake support the hypothesis that CO hydrogenation proceeds over anion vacancy sites.

The data in Tables 1 and 2 show that as the ZrO_2 (samples 1-6) was calcined at higher temperatures or for longer times the amount of interaction of the various probe molecules increased. Transmission electron microscopy studies revealed that the ZrO_2 grain morphology changed from irregular to more or less equiaxed and polygonal with increasing severity of calcination. The yttria doped samples calcined at 600 °C had grains similar to the least sintered ZrO_2 samples (samples 1 and 2), and unexpectedly had a lower uptake than the pure ZrO_2 samples. The sintering studies with the yttria doped zirconia (samples 9 and 9', 11 and 11', and 15 and 15') were done to determine if grain morphology influenced the uptake. Figure 6 demonstrates that, for similarly calcined samples, the maximum uptake appeared at the dopant level of maximum conductivity, providing additional support for the vacancy-conductivity argument [6] presented above. The sintered and unsintered yttria doped samples are identified in Figure 5. These points show that sintering, which affects the grain morphology, causes the uptake of the various probes to increase and alters the surface density of vacancies. (We did not study how sintering altered the density of vacancies.)

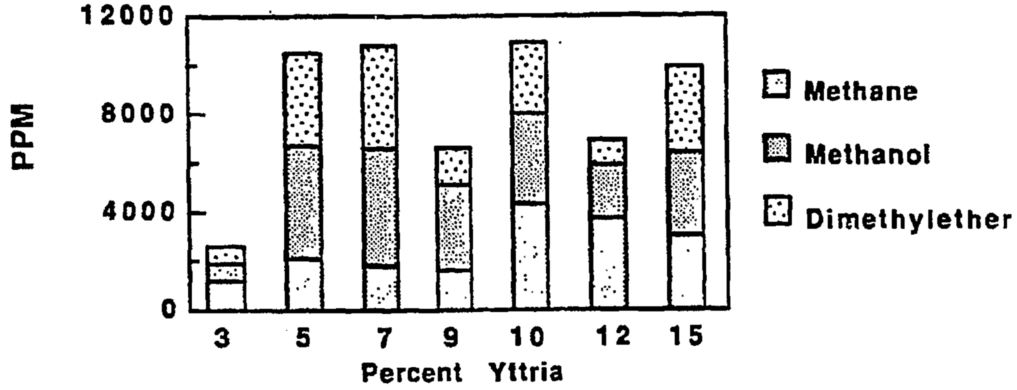
Isosynthesis Mechanisms and Selectivity The reactions are shown in Figures 2 and 3. Study of the isosynthesis reaction is complicated because: (1) C_3 and higher surface intermediates can participate in two different chain growth steps, (2) both chain growth steps can lead to branched products, and (3) there are intermediates which are common to both chain growth steps and it is difficult to associate a particular product with a unique sequence of surface reactions. We established the reactions shown in Figures 2 and 3 by using ^{13}C-labelled reactants [5] which adsorbed to generate key intermediates and form products by only one of two possible reactions. The condensation reaction is what presumably causes the isosynthesis product distribution to deviate from the typical Flory distribution observed for Fischer-Tropsch synthesis. (Flory plots for isosynthesis show a discontinuity at C_4; the curves have a step increase because the second chain growth step, condensation, begins contributing to these products.) Below we use a number called the isosynthesis profile, $C_4/(C_2+C_3)$, to indicate the presence of two chain growth reactions.

To determine the surface characteristics that cause a metal oxide to have the unique selectivity of the isosynthesis reaction 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. Preliminary results indicate that zirconia's selectivity as a CO hydrogenation catalyst comes from a unique and necessary combination of surface properties: acid sites, basic sites, and mobile oxygen vacancies. The acid sites are required for condensation. The oxygen vacancies influence the condensation reaction. The basic sites are required for the CO insertion reaction. This study will be completed during the current grant period by examining the selectivity for 2-alcohol dehydration and relative rates of CO insertion and methoxide condensation using ^{13}C-labelled acetone and methanol. At the completion of these studies definite conclusions will be possible and we anticipate submitting at least two manuscripts for publication.

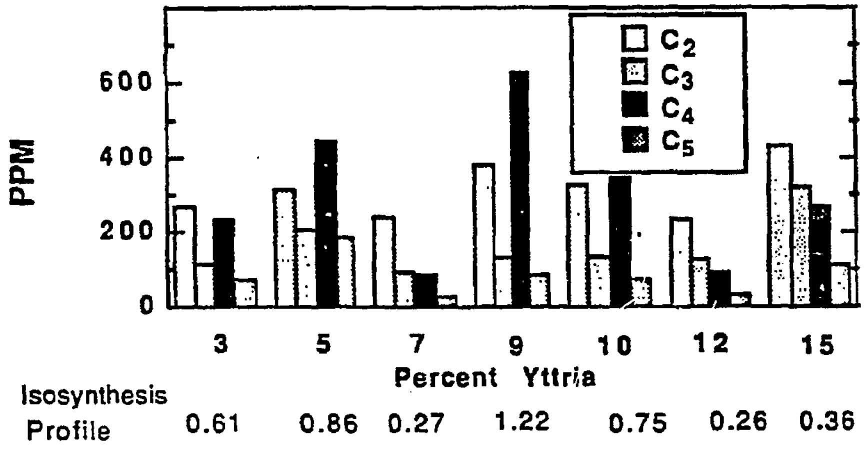
Figures 7 and 8 are representative of the activity and selectivity patterns with yttria and calcia dopants and can be used to examine the role of oxygen ion mobility. Both series of doped catalysts showed the greatest branched-to-linear ratio at the percentage of dopant known to have the largest electrical conductivity (ca. 9% Y_2O_3 and 13% CaO). The isosynthesis profile is generally found to increase with oxygen vacancy mobility, suggesting that the condensation reaction is enhanced by increased oxygen vacancy mobility.

Figure 9 presents the effect of acidity on the isosynthesis reaction.

Methoxide Products over Yttria Stablized Zirconia Catalysts



Hydrocarbon Production over Yttria Stablized Zirconia Catalysts



Branched-to-Linear Ratio over Yttria Stablized Zirconia Catalysts

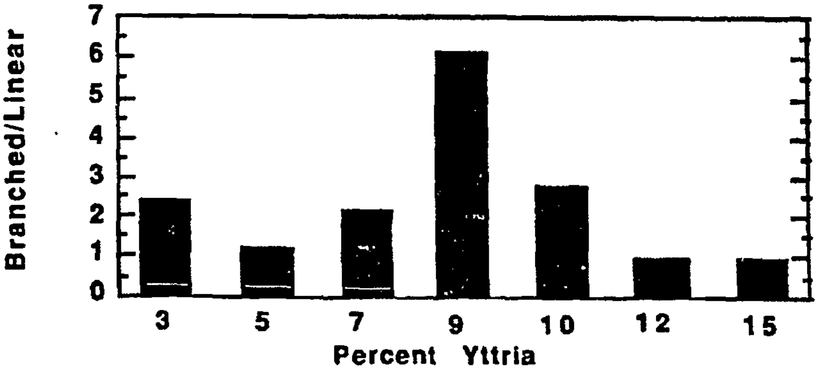
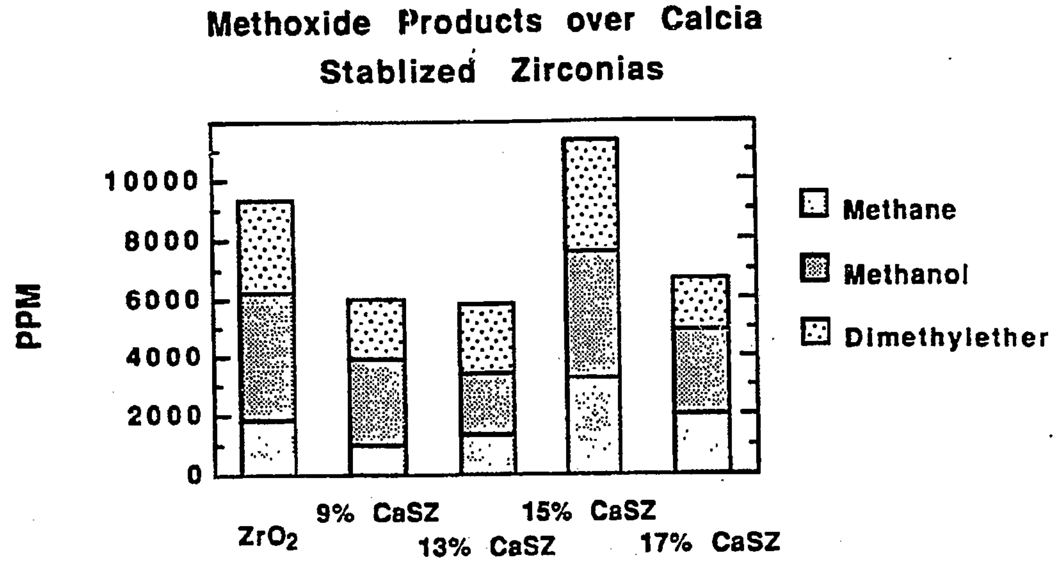
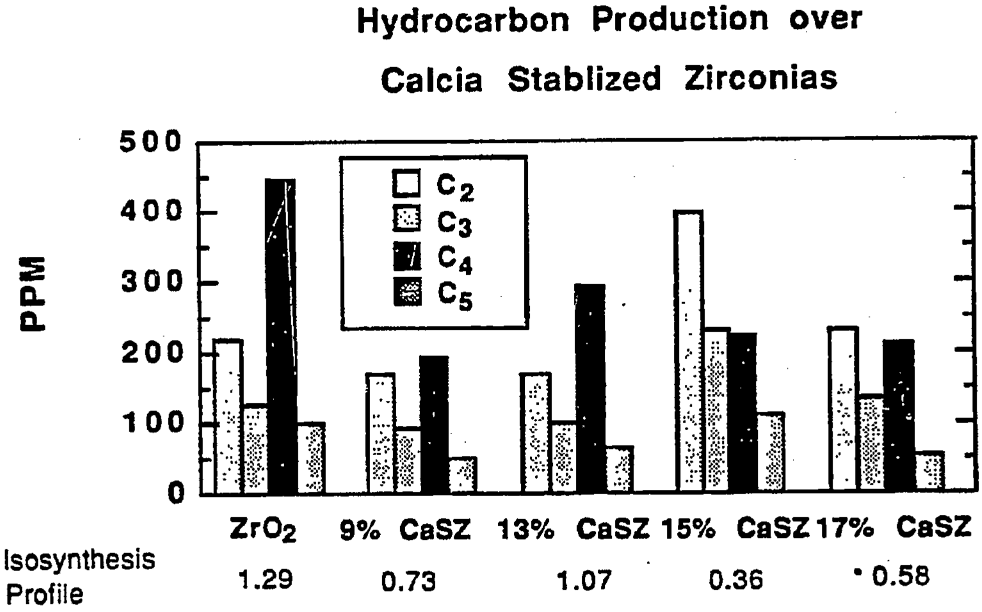


FIGURE 7


Methoxide Products over Calcia Stablized Zirconias


Hydrocarbon Production over Calcia Stablized Zirconias

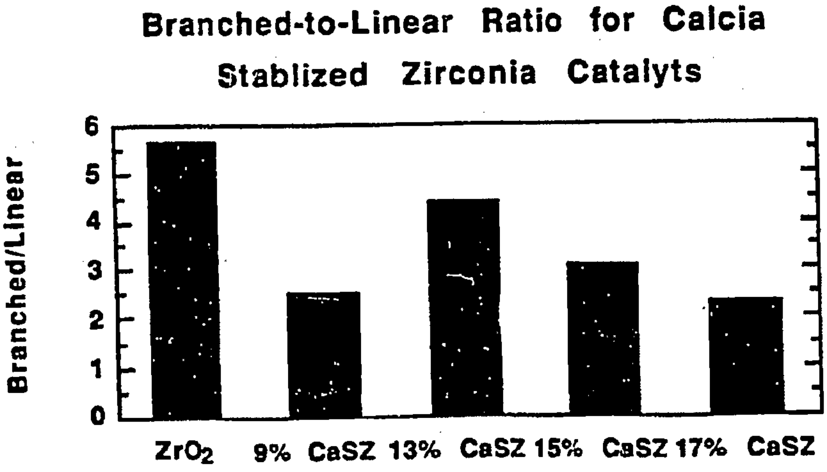
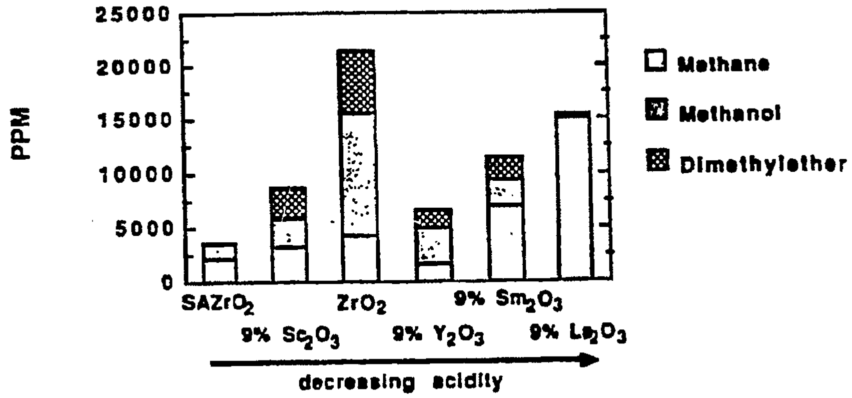
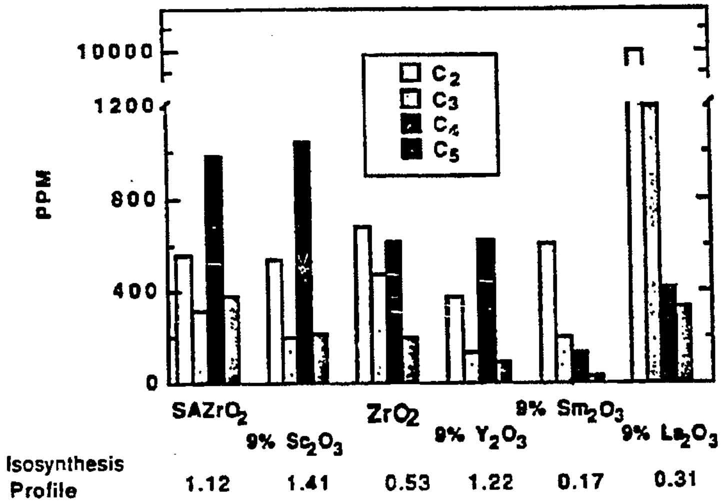

Branched-to-Linear Ratio for Calcia Stablized Zirconia Catalyts

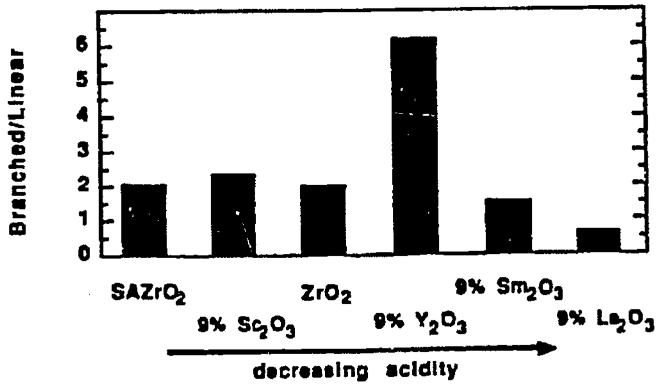
FIGURE 8



Methoxide Products over Zirconia and Zirconia-Mixed Oxide Catalysts



C$_2$ - C$_5$ Hydrocarbon Production over Zirconia-Mixed Metal Oxides



Branched-to-Linear Ratio for Zirconia and Zirconia-Mixed Metal Oxide Catalysts

FIGURE 9

SAZrO_2 refers to super acid zirconia made by soaking the ZrO_2, shown in Figure 9, in sulfuric acid. The most acidic catalysts have the largest isosynthesis profile. As the catalysts get less acidic, their overall conversion increases. Experiments over ZrO_2 [5] found that the addition of $^{13}CH_3OH$ resulted in the inclusion of ^{13}C only in branched products, leading us to conclude that condensation only resulted in branched products. (This is also equivalent to stating that there was a very low concentration of adsorbed methyl ketones which could convert into an enolate and undergo condensation.) However, the acidic catalysts tested that have a high isosynthesis profile do not also have relatively large branched-to-linear ratios. ^{13}C-labelled methanol will be used to determine whether the condensation reaction leads to straight chain as well as branched products over the more acidic catalysts.

Figure 9 also reveals the effect of basicity on the isosynthesis reaction. The most basic catalyst, 9% La_2O_3, was the most active and had the least branching. Poisoning experiments with CO_2 to block the La sites with carbonate reveal a reversible transformation of the lanthana doped ZrO_2 into a catalyst that has the same selectivity pattern as undoped ZrO_2. This suggests that basic sites influence the CO insertion reaction.

The means by which acidity and basicity affect selectivity will be determined by injecting varying amounts of ^{13}C-labelled acetone and methanol into the synthesis gas mixture. Incorporation of the isotopic reactant into the isosynthesis products and changes in extent of incorporation will be used to address several specific questions. We will also study the selectivity of 2-alcohol dehydration.

Figure 10 can be used to illustrate how the ^{13}C-labelled methanol and

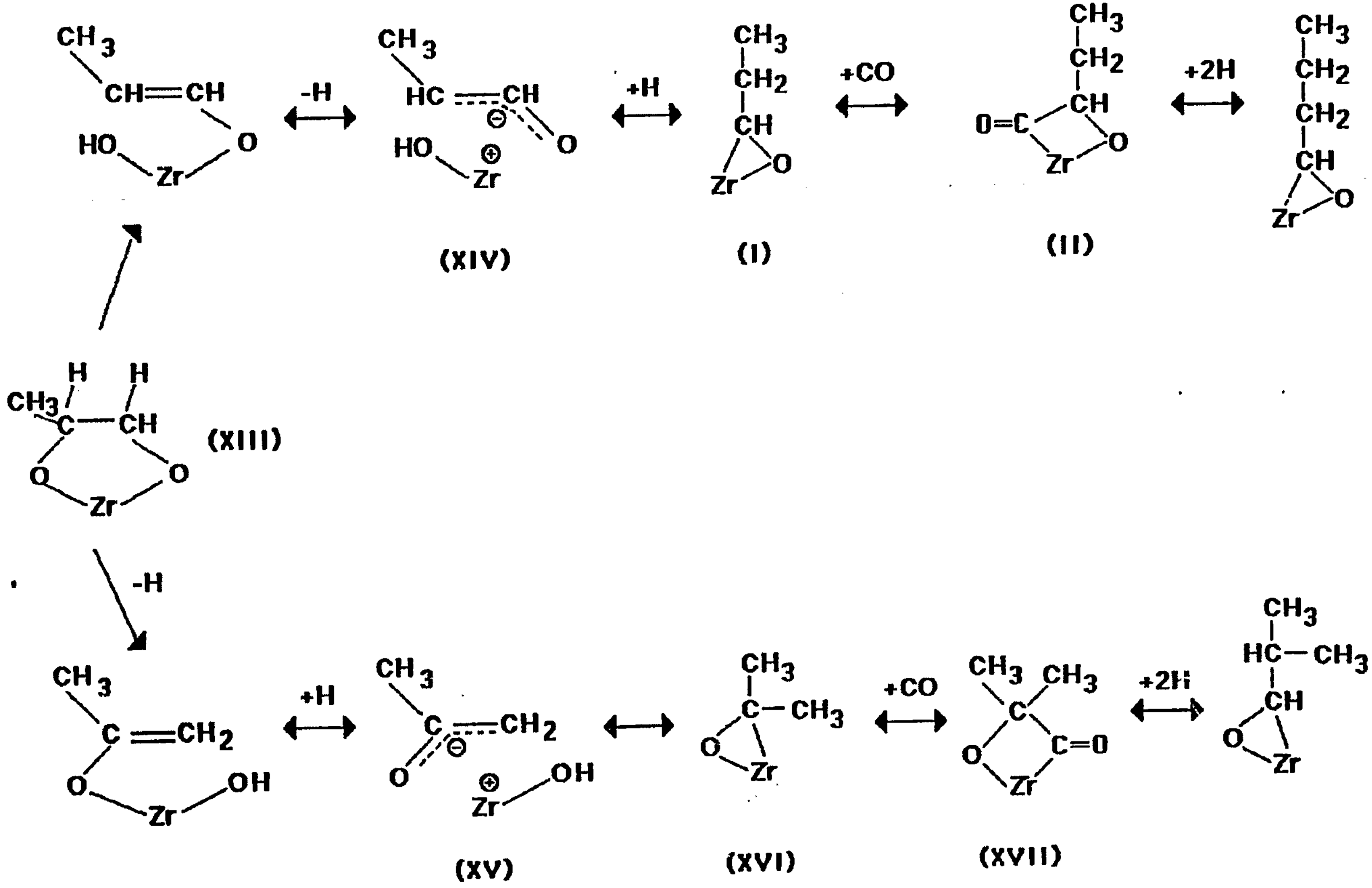


FIGURE 10

acetone will provide insight into the effects of acid/base additives and anion vacancies on the isosynthesis reaction intermediates. Figure 2 presents the CO insertion reactions leading to C_4 products; a 1,2-butanediolate (VI) is formed and is shown reacting to enolate VIII. The 1,2 diolates can react to two different enolates. (Only one path was shown in Figure 2.) The 1,2-propanediolate (XIII), shown in Figure 10, would form from CO insertion into acetaldehyde and react to enolates XIV and XV. The amount of $^{13}CH_3OH$ incorporating into linear butenes (by reaction with XV) and isobutene (by reaction with XIV) will enable us to probe how the additives influence the relative concentration of these two enolates. Enolates XIV and XV provide a relative measure of the adsorbed aldehydes (I and XVI) which undergo CO insertion. The methanol studies will be used to ascertain what causes changes in the isosynthesis profile and branched-to-linear ratio. In our earlier study [5] we used changes in the amount of acetone incorporation into linear and branched butenes to determine the relative rate of CO insertion and condensation for XVI. We will employ a similar approach over the catalysts discussed above to determine if the relative rates change as acidity and anion vacancy concentration changes.

Figure 11 presents a scheme for 2-alcohol dehydration [14]. We will determine how the additives affect the selectivity to 1-butene as a means of gaining insight into those catalytic properties which stabilize enolate VIII. Enolate VIII is one of two possible products from 1,2-butanediolate (Figure 2). The dehydration study will help us to determine if the alternate enolate (the C_4 analog of XIV) is more favored during CO insertion.

We expect to complete the dehydration and ^{13}C-labelled reactant studies within the next two months. The isosynthesis results illustrated in Figures

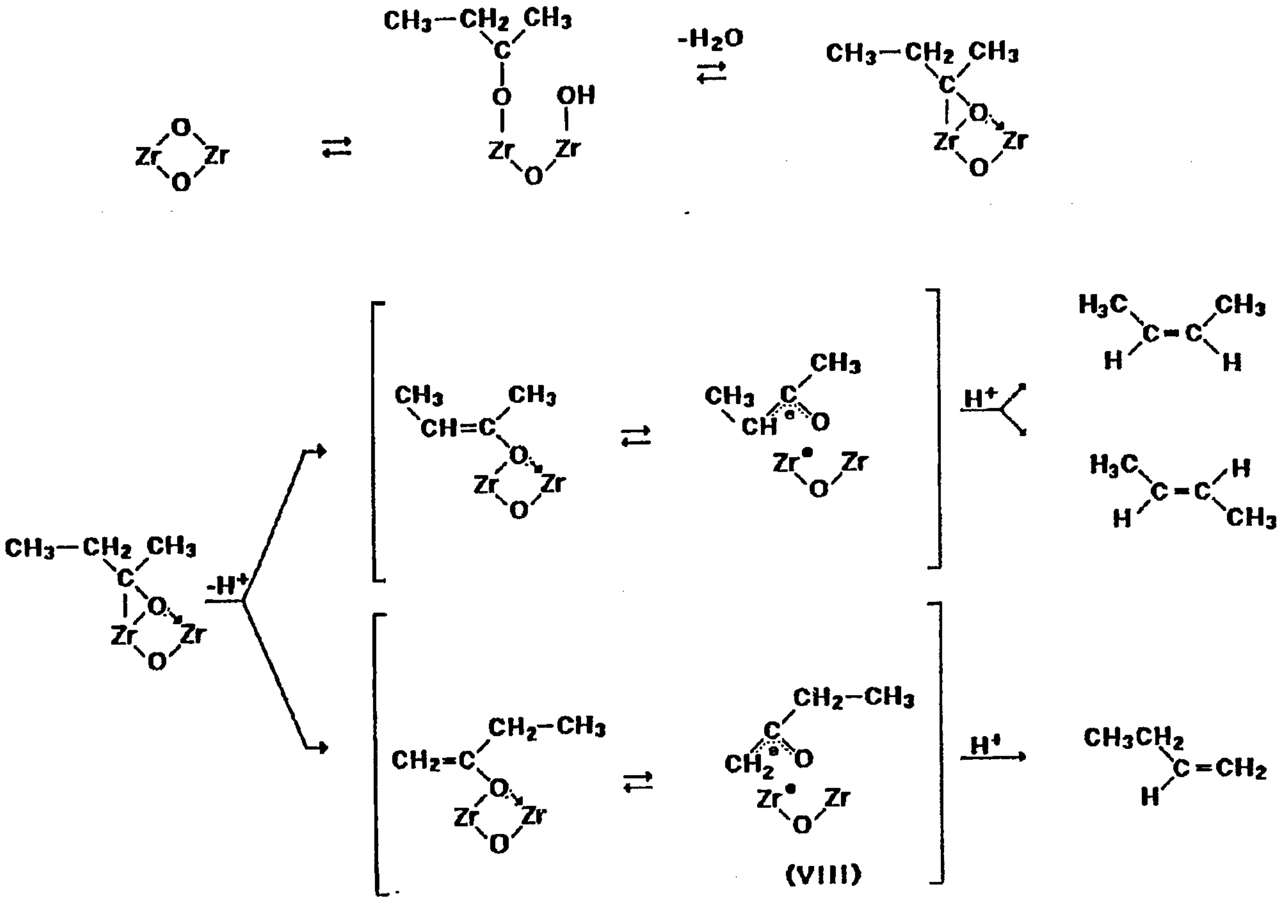


FIGURE 11

7-9 have identified the catalyst systems over which each of these probe reactions should be conducted. We will not perform the labelled studies over all the systems we have prepared because the cost of the compounds is prohibitive.

DIRECTION OF FUTURE WORK

During the course of our studies we have determined that a key limitation to developing insight into how oxides function in catalytic reactions is in not having precise information of the surface composition under reaction conditions. (We were able to identify how basicity, oxygen anion vacancy concentration and oxygen vacancy migration affect the absolute activity and selectivity to hydrocarbons and alcohols. However, we were only able to infer the surface site at which the reactions occurred (anion vacancies) and were unable to control the surface composition or structure beyond altering the bulk oxide composition.) To address this problem we have initiated the synthesis of oxide systems which can be used to model oxide catalysis in a systematic fashion. Since many oxide catalyst systems involve a mixture of oxides, we have selected a model system which will permit us to examine the role of each cation separately and in pairwise combinations. This research is based on the work of Iwasawa [15-19] in which organometallic mononuclear and dinuclear Mo complexes have been used to support atomically dispersed monomers and dimers of Mo on silica and alumina. The oxidation state of the isolated monomers and dimers can be changed and, in principle, one thereby has a system in which all cations have the same structure and oxidation state. The aspect of pairwise cation-cation effects in mixed oxide catalysts can be addressed by using heterobimetallic organometallic complexes. We have initiated the synthesis and deposition of Mo_2, W_2 and MoW organometallic complexes, with which silica- and alumina-supported model oxide catalyst systems can be prepared. This research is discussed in detail in the renewal proposal.

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GRADUATE STUDENTS SUPPORTED BY DOE

M. A. Barker - M.S. (1983)	"Conversion of Synthesis Gas Over Zirconia"
N. B. Jackson - M.S. (1985)	"Studies of CO Interaction with Zirconia and Methanol Synthesis Mechanisms"
C. J. Wang - Ph.D. (1983)	"Study of Fischer-Tropsch Synthesis over a Silica Supported Iron Catalyst Through the use of Reactive Scavengers"
K. G. Anderson - Ph.D. (1987)	Initially began working on a M.S. degree and was involved with reactive scavenging using amines. He switched projects because we stopped investigating Fischer-Tropsch synthesis.
S. C. Tseng - Ph.D. (1987)	"Isosynthesis Reactions of CO/H_2 over Zirconium Dioxide"
N. B. Jackson - Ph.D. (1989) (expected)	"Isosynthesis over Metal Oxide Catalysts"
R. G. Silver - Ph.D. (1989) (expected)	"A Study of Active Sites for Isosynthesis over Zirconium Dioxide"
R. D. Roark - Ph.D. (1992-93)	

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