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The Surface Characteristics Required for Isosynthesis over Zirconium Dioxide and Modified Zirconium Dioxide

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The surface requirements for the two isosynthesis chain growth reactions, condensation and CO insertion, over zirconium dioxide were studied by modifying zirconium dioxide in controlled ways and studying the effects of these changes on the isosynthesis reaction products at 425°C and 35 atm. The oxygen vacancy availability was altered by the addition of dopants Y_2O_3 and CaO at various levels. The acid/base strength of the catalysts was altered by additives including H_2SO_4, Sc_2O_3, Y_2O_3, and Sm_2O_3. Calcination methods and temperatures for ZrO_2 were varied. Lewis acid sites and oxygen vacancies were found to enhance the condensation reaction. The CO insertion reaction was enhanced by basic sites which were activated by high-temperature treatment. The selectivity of the isosynthesis reaction is caused by a balance between the strength and quantity of acid and base sites on zirconium dioxide.

I. INTRODUCTION

The synthesis gas reaction over zirconium dioxide, isosynthesis, has been studied in depth recently in this laboratory (*1–7*) and by others (*8–10*). Extensive C_1 data have been published and a mechanism for methanol formation has been proposed by a number of workers that involves a formate-to-methoxide mechanism (*1–3, 11, 12*). Methoxide leads to both methane and methanol. However, methanol forms only in the presence of water, and methane may be formed from CO and H_2 only (*4*). Dimethylether is also formed from a methoxide precursor (*3*). Two chain growth mechanisms have been proposed (*5*) for reactions leading to C_{3+} hydrocarbons over zirconium dioxide and these account for the unique selectivity toward branched hydrocarbon product distributions over zirconium dioxide. The two chain growth mechanisms include CO insertion and a condensation reaction. See Fig. 1.

The CO insertion reaction involves the insertion of CO into an aldehydic surface intermediate. CO insertion leads to the formation of an enol (I) which can lead to two possible η^3-enolates (II and III) which upon hydrogenation become isomeric aldehydic surface intermediates—branched and linear (IV and V)—capable of desorption or further reaction. Since CO insertion is an α-addition reaction, continued CO insertion would lead to both branched and linear hydrocarbons (*5, 13*). The stability of the two η^3-enolates (II and III) relative to the aldehydic intermediates determines the relative number of branched-to-linear C_4 products from the CO insertion reaction (*13*).

The surface requirements for the CO insertion reaction are not well understood. Enols are known to be stabilized by coordination to a saturated and sterically congested Th^{4+} center (*14*). (Thorium dioxide is also an active isosynthesis catalyst.) The acid/base nature of metal oxides has been suggested to play a role in branched hydrocarbon formation by the CO insertion reaction. Mazanec suggested that the η^3-enolate was also an intermediate in the dehydration reactions of alcohols over basic catalysts such as ThO_2 (*13*). The relative stability of the two enolates formed from 2-alcohols de-

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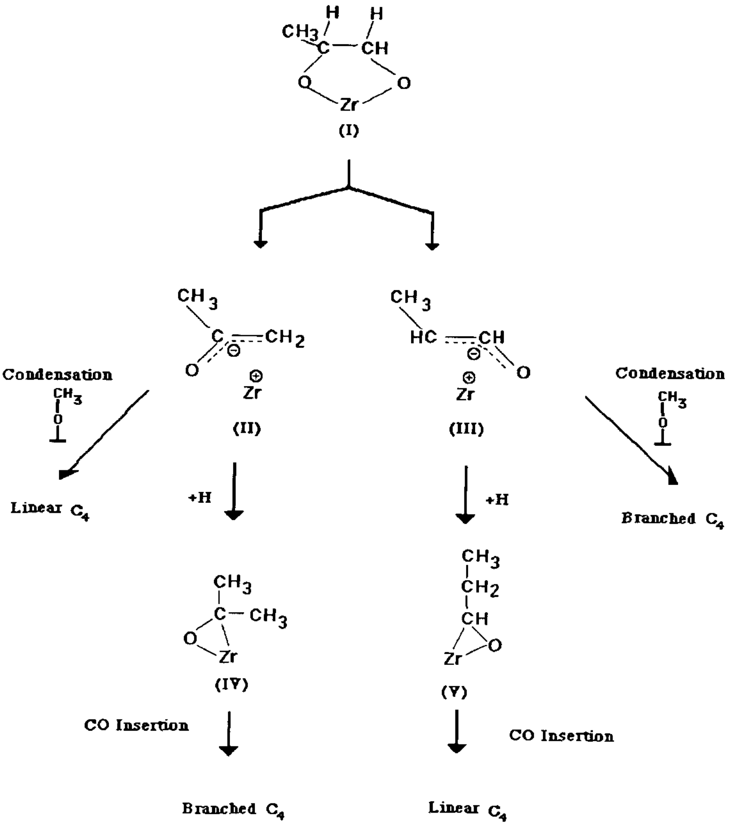

FIG. 1. Four possible reaction paths to the formation of C_4 species over zirconium dioxide. One C_3 intermediate I, a cyclic acyl, leads to two possible enolates, II and III, which may either react with a methoxide in a condensation reaction or react to form an adsorbed ketone IV or aldehyde V and then undergo CO insertion (*5*).

termined the relative amount of 1-olefins versus 2-olefins. The basic nature of catalysts such as CaO, MgO, and ThO_2 was credited for the unique selectivity to 1-olefins through stabilization of enolates similar to II. The more basic the catalyst, the greater the selectivity toward 1-olefins over 2-olefins from 2-alcohols (*15–17*). Since it has been suggested (*13*) that the enolate leading to 1-olefins in the dehydration has the same structure as the enolate, II, that leads to branched hydrocarbons by CO insertion, the basicity of the catalyst may contribute to the abundance of branched isosynthesis products.

The second chain growth mechanism involves a condensation reaction between a methoxide and an η^3-enolate. Since condensation is a β-addition reaction, condensation between a methoxide and II leads to a linear aldehydic species and condensation between a methoxide and III leads to an adsorbed ketone branched species. These species may either desorb as linear or branched hydrocarbons or may react further by CO insertion or condensation. Recent work (*5*) with $^{13}CH_3OH$ addition to the isosynthesis reaction over zirconium dioxide showed that the condensation reaction leads primarily to branched hydrocarbons. The amount of labeled methanol incorporating into C_3 products was found to be 42% (*18*) and 34% (*19*) of the amount incorporating into 2-methylpropene; therefore, it was concluded that the condensation reaction is more significant with C_3 enolates than with C_2 enolates (suggested by Mazanec (*13*)), and explains the deviation of the isosynthesis product distribution from the typical Schulz–Flory distribution observed for Fischer–Tropsch synthesis. Schulz–Flory plots for isosynthesis over ZrO_2 show a discontinuity at C_4; the curves have a step increase because a second, competing chain growth step, condensation, is also contributing to these products (*20*). Klier and coworkers (*21*) suggested that the condensation mechanism found on alkali promoted Cu/ZnO catalysts is similar to aldol condensation over basic metal oxides. Since both isosynthesis reactions, CO insertion and condensation, appear to share features with basic catalyzed reactions, the acid/base nature of the catalyst surface may be crucial to the isosynthesis activity.

The availability of alkoxides on the surface of metal oxides has been suggested as the factor which makes the condensation reaction a significant contributor to isosynthesis product formation (*13*). The surface requirements for methoxide formation have been proposed (*4*) and studied (*6*). The surface site required for methoxide formation was identified as an oxygen vacancy. Since methoxide is instrumental in the condensation reaction it would follow that the number or availability of oxygen vacancies might have an effect on the isosynthesis products. Oxygen vacancies may play an even more significant role in the isosynthesis reaction than just methanol formation since a unique trait shared by the two most active isosynthesis catalysts, thorium dioxide and zirconium dioxide, is that they are both known to have oxygen vacancies (*22*). The relative number of oxygen vacancies can be controlled by the direct substitution of varying amounts of di- or trivalent cations of appropriate size 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. These vacancies increase the electrical conductivity, with diffusing oxygen ions being the primary charge carrier (*22–24*). This diffusion of oxygen has been associated with lattice vacancy migration (*22, 23*). For the case of yttrium oxide doped zirconium dioxide, spectroscopic studies have shown that the trivalent and tetravalent cations are statistically distributed (*25*) and that the Zr^{4+} cations are nearest neighbors to the anion vacancies (*26*). Additional studies (*6*) have shown the surface and bulk yttrium cation concentrations to be similar.

The oxides of zirconium form three different phases: monoclinic, tetragonal, and cubic (*27–29*). The monoclinic phase is stable below 1200°C, and the cubic phase is formed at temperatures above 2280°C and has a fluorite crystal structure. However, creating a solid solution of zirconium dioxide with di- or trivalent cations such as Ca^{+2}, Y^{+3}, Sc^{+3}, or Sm^{+3} causes the stabilization of the cubic crystal structure of zirconium dioxide at room temperature. The amount of dopant required for stabilization of the cubic crystal structure varies depending upon the dopant. Below the required level, a mixture of tetragonal and cubic crystal structures are formed. For a solid solution of yttria in zirconium dioxide the exact crystal structure of the mixture can be predicted knowing the concentration of yttria present (*30*). The calculated phase mixture would not be accurate if the two oxides were not in solution. For the yttrium oxide–zirconium oxide samples used in this study the crystal structure found by X-ray diffraction was what was expected from the starting ratio of yttria and zirconia salts (see below). For information on the doped zirconium dioxides used in this study, see Table 1. The electrical conductivity maximum occurs just beyond the dopant level where the cubic phase is fully stabilized (*22, 31*). Also, studies of M_2O_3–ZrO_2 mixtures have shown that generally, electrical conductivity increases as the size of the dopant cation decreases (*31*).

Zirconium dioxide is considered a bifunctional catalyst with both acidic and basic sites (*32, 33*). Pretreatment temperature has

TABLE 1

Metal Oxide Stabilizers for Cubic Zirconia[a]

	Lower phase boundary for cubic fluorite structure (mol% oxide dopant)	Maximum conductivity (mol% oxide dopant)
Sc_2O_3	6	8–12
Y_2O_3	7–8	9–10
Sm_2O_3	7	10
CaO	12–13	12–13

[a] Data from Ref. (*22*) and references therein.

been shown to have an effect on the acid–base properties of zirconium dioxide. The effect of acid–base and oxidizing-reducing properties of zirconium dioxide pretreated at various temperatures on the isomerization of 1-butene was studied (*32*). The isomerization reaction was found to be active on zirconium dioxide pretreated at as low a temperature as 400°C and activity increased with increasing pretreatment temperature up to a maximum of 800°C. Activity then fell off rapidly for pretreatment above 800°C. Strong basic sites (measured by adsorption of diphenylamine) correlated best with the activity for 1-butene isomerization. A maximum of strong basic sites was found on zirconium dioxide pretreated at 700°C. However, a maximum of strong acidic sites (measured by NH_3) adsorption was also found at 700°C.

The purpose of this present study is to identify surface requirements for isosynthesis reactivity and selectivity. The method used was to alter the zirconium dioxide catalyst in controlled ways and then study the effects of these changes on the isosynthesis reaction products in order to determine the surface requirements for the two chain growth reactions, CO insertion, and condensation. The three alterations to zirconium dioxide include (1) doping zirconium dioxide with various quantities of M^{+2} and M^{+3} cations to study the effect of oxygen vacancies and oxygen vacancy mobility; (2) adding dopants of varying acidity to determine the effect of surface acidity and basicity; and (*3*) varying catalyst pretreatment to study the effect changes of surface preparation have on both reactions.

II. METHODS

Catalyst preparation. The zirconium dioxide catalysts were prepared from a solution of chloride salts which were precipitated with NH_4OH to form a hydroxide gel. (NaOH was used in place of NH_4OH for any solution containing calcium since ammonia complexes with calcium in solution preventing complete precipitation.) The precipitates were rinsed until their wash water tested negative for chloride ion with $AgNO_3$. The gel was dried at 120°C for 24 h and then calcined for 4 h at 600°C in hydrocarbon-free air to give a high area (35–110 m^2/g) oxide. The concentration of the additive, such as Y_2O_3, was changed in a systematic manner by changing the ratio of Zr and Y in the salt solution. The N_2 BET surface area and the X-ray diffraction pattern were taken for each catalyst. These results are listed in Table 2. The percents tetragonal and monoclinic, determined from the X-ray diffraction patterns, match those predicted for solution of the respective dopants in ZrO_2 (*6, 30*). X-ray photoelectron spectroscopy (XPS) analysis of ZrO_2–Y_2O_3, ZrO_2–Sc_2O_3, and ZrO_2–CaO catalysts revealed the surface and bulk compositions were similar and no surface segregation of the dopants was found (*19*).

Acid-modified zirconium dioxide ($AZrO_2$) was made by contacting zirconium dioxide with sulfuric acid. After drying zirconium dioxide for 24 h at 120°C the zirconium dioxide was allowed to sit in a solution of 0.1 *M* H_2SO_4. The treated catalyst was then dried overnight at 120°C and calcined for 4 h in hydrocarbon-free air at 600°C. This method of synthesis was adapted from Ref. (*34*).

Calcination methods. All catalysts were calcined at 600°C in hydrocarbon-free air for 4 h, but some were calcined additionally as well. Calcination Method A involved calcining the catalysts in the reactor in flowing

TABLE 2

Surface Area and Phase Composition for Zirconium Dioxide Catalysts

Catalyst	BET N_2 Surface area (m^2/g)	Phase[a] (M/T/C)
ZrO_2	77	93/7/0
3.3% Y_2O_3[b]	59	0/90/10
5.0% Y_2O_3	62	0/56/44
7.0% Y_2O_3	74	0/20/80
9.1% Y_2O_3	75	0/0/100
9.8% Y_2O_3	95	0/0/100
11.8% Y_2O_3	63	0/0/100
15.0% Y_2O_3	82	0/0/100
9% CaO	91	0/0/100
13% CaO	105	0/0/100
15% CaO	102	0/0/100
17% CaO	97	0/0/100
9% Sc_2O_3	48	0/69/31
9% Sm_2O_3	70	0/0/100
$AZrO_2$[c]	28	91/9/0
ZrO_2[d]	23	96/4/0
ZrO_2[e]	23	95/5/0
ZrO_2[f]	21	100/0/0
ZrO_2[g]	19	100/0/0

[a] Percentage of monoclinic, tetragonal, and cubic phases present.

[b] Mol% remainder is always ZrO_2.

[c] ZrO_2 modified with H_2SO_4.

[d] Calcined Method A for 1 h at 750°C in O_2.

[e] Calcined Method A for 1 h at 800°C in O_2.

[f] Calcined Method B for 1 h at 750°C in air.

[g] Calcined Method B for 1 h at 800°C in air.

oxygen for 1 h immediately before isosynthesis. Calcination Method B involved calcining the catalysts for 1 h in hydrocarbon-free air and then storing the catalyst until needed. These catalysts were then pretreated in O_2 for 10 min at 600°C to remove any carbonates or water adsorbed upon storage.

Materials. The oxide starting materials were purchased from Alfa Products. They include $ZrCl_4$ (99.6%), YCl_3 (99.9%), $Sc(NO_3)_2$ (99.9%), Sc_2O_3 (99.9%), $ScCl_3$ (99.9%), and Sm_2O_3 (99.9%).

Hydrogen (99.999%) and CO (99.9%) were purchased already mixed at a 50/50 ratio ±0.2% from Wilson Oxygen. The synthesis gas mixture and He (99.995%) were purified by passing through O_2 absorbing filters and molecular sieve filters to remove water. The O_2 (99.995%) was purified with a molecular sieve filter. Prior to reaching the reactor, the CO/H_2 mixture was heated to 200°C to remove any carbonyls.

Apparatus. The reactor was 28-cm long and made out of 0.533-cm i.d. 316 stainless-steel tubing. Two grams of catalyst were used for each reaction and the catalyst bed length varied from 5 to 8 cm depending upon the density of the catalyst. All tubing was made out of 0.318-cm o.d. stainless steel, except the CO/H_2 tubing which was made out of copper. Gases were heated to 150°C before entering the reactor. Products were analyzed on a Hewlett Packard 5890A gas chromatograph using two separate columns. Reactor effluent was directed to a 1-ml sample loop which allowed direct injection into a 25 m × 0.53 mm BP-1 megabore, aluminum coated column (Scientific Glass & Engineering Co.). The nonpolar BP-1 column had a 5-μm coating of dimethyl siloxane and could be used to separate most C_1 through C_5 compounds. Oxygenates such as 2-butanol and isobutyraldehyde could also be monitored on this column; however, no significant amounts of these compounds were ever formed. To complete the analysis, a gas-tight syringe was used to inject 300 μl of reactor effluent into a 0.318-cm-o.d. × 2.74-m stainless-steel column packed with 0.19 wt% picric acid on 80/100 mesh Carbopack C (Supelco) in order to separate 1-butene from 2-methylpropene. A complete list of products monitored can be found in Ref. (*5*).

Procedure. All isosynthesis reactions used 2 g of catalyst. Each catalyst was pretreated at 600°C in flowing oxygen for 10 min and then cooled in helium. The 50/50 mixture of CO/H_2 was passed over the catalyst at 100 sccm at 500 psi. The reaction temperature was 425°C and, unless stated otherwise, each reaction was allowed to come to steady state for 2 h before analysis began.

Alcohol dehydration experiments used 2

g of catalyst pretreated at 600°C in O_2 for 10 min and then cooled in He. An 80/20 mixture of 2-butanol/2-hexanol was pumped into the reactor with a HPLC syringe pump (Isco Model μLC-500) at a rate of 40 μl/min with a helium flow of 45 sccm at 500 psi. The dehydration experiments took place at 400°C. 1-Butene and *cis*- and *trans*-2-butene were the major products, and they were analyzed with the picric acid column. 2-Hexanol was added in order to prevent secondary reactions, the most common one being 1-butene isomerizing to 2-butene (at 400°C the equilibrium mixture of linear butenes is 24% 1-butene, 30% *cis*-2-butene and 46% *trans*-2-butene). The lower vapor pressure of the 2-hexanol helped to keep surface sites covered, lowering the chance of secondary reactions (*35*).

III. RESULTS

In order to study the effect of the number and mobility of oxygen vacancies, two series of doped zirconium dioxides were prepared. Seven yttria-doped zirconium dioxides (3.3, 5.0, 7.0, 9.1, 9.8, 11.8, and 15.0 mol% Y_2O_3) and four calcia-doped zirconium dioxides (9.0, 13.0, 15.0, and 17.0 mole percent CaO) were tested for their isosynthesis activity. The results are shown in Figs. 2 and 3. Note the shape of the C_2–C_5 hydrocarbon production graphs, particularly the large step increase in C_4 production for 100% ZrO_2 and many other catalysts. This increase was due to the introduction of the second chain growth reaction, condensation, that contributes to the formation of C_4 and higher hydrocarbons (*5*). To gauge the relative importance of the condensation reaction, we use a number called the isosynthesis profile ($C_4/(C_2 + C_3)$). This number has varied over zirconium dioxide and ZrO_2-mixed metal oxide catalysts from a high of 1.41 to a low of 0.17.

Both the calcia-doped zirconium dioxide and the yttria-doped zirconium dioxide showed a clear maximum in isosynthesis profile and branched-to-linear ratio. (In this paper, branched-to-linear ratio refers to the ratio of C_4 and C_5 branched-to-linear products.) The maximum was at 9.1% Y_2O_3 and 13% CaO. The branched-to-linear ratio and the isosynthesis profile correlate, in general, with each other for the yttria- and calcia-doped catalysts. The C_1 production for the maxima points was low. The quantity of methoxide products formed was not related to the percentage of dopant. In addition, distribution among methoxide products remained consistent no matter what percentage dopant was used. Pure calcia and yttria were also tested for their isosynthesis activity. The branched-to-linear ratio and isosynthesis profile for CaO was 0.343 and 0.193, and for Y_2O_3 was 0.670 and 0.305. Both calcia and yttria showed virtually no dimethylether formation. On a per area basis, CaO was 8.5 times more active and Y_2O_3 was 1.4 times more active than ZrO_2 for C_1–C_5 hydrocarbon production; and CaO was 17.7 times more active than ZrO_2 for C_2–C_5 hydrocarbon production. The isosynthesis profile of the 7% Y_2O_3 catalyst appeared low in comparison with the other yttria catalysts. This was not a deviation due to experimental error. This catalyst was synthesized twice and tested a number of times with similar results. It is not clear what caused the 7% Y_2O_3 catalyst to be so inactive toward the condensation reaction.

Variations in activity and selectivity were noted between batches of catalyst. Each batch of zirconium dioxide synthesized showed a slightly different selectivity although they all remained within a certain range that was characteristic of the isosynthesis reaction (high isosynthesis profile, high branched-to-linear ratio). The isosynthesis profile was known to deviate up to 15% from the average isosynthesis profile value for all zirconium dioxide catalysts used in Ref. (*20*) and this study. All catalyst batches were made and calcined identically; however, surface area (33–76 m^2/g) and percent monoclinic/tetragonal (89–93% monoclinic) varied for each zirconium dioxide catalyst produced. Neither the percent monoclinic present nor the surface area ap-

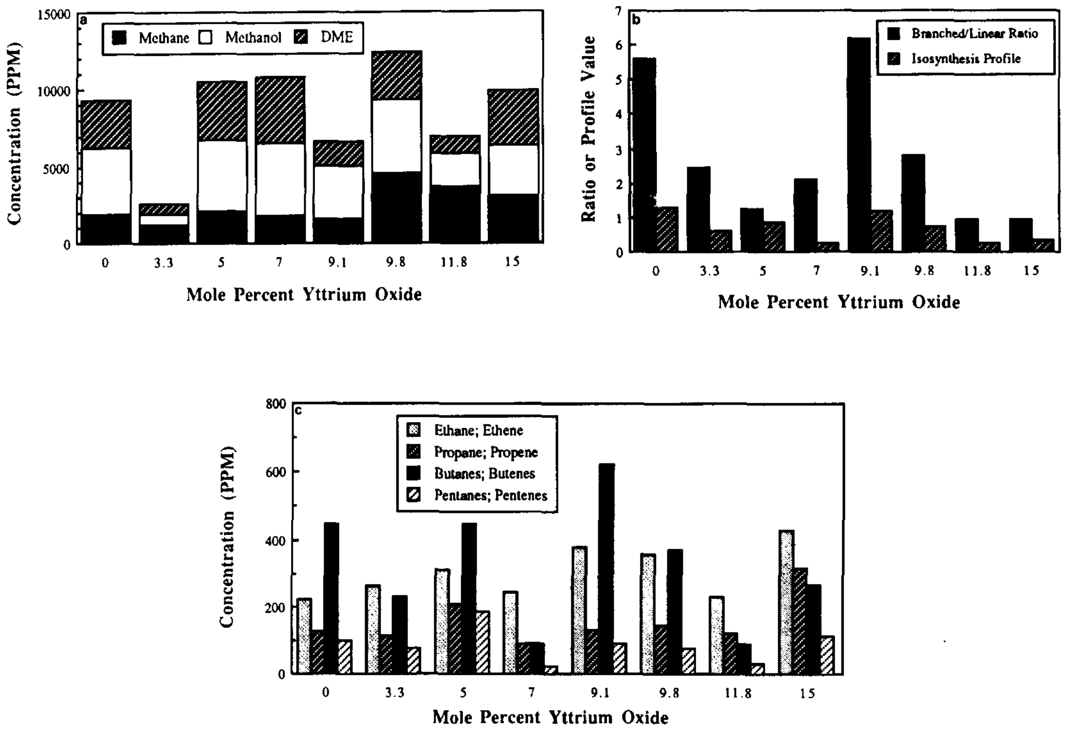

FIG. 2. Isosynthesis product formation over ZrO_2 and ZrO_2–Y_2O_3-mixed oxide catalysts. Branched/linear ratio is for C_4 and C_5 species only.

peared to have an identifiable influence on either the activity or the isosynthesis profile. The zirconium dioxide shown in Figs. 2 and 3 was a mixture of five catalyst batches. Most of the catalysts in this study were synthesized at least twice and data shown for each catalyst are an average of many experiments.

To study the effect of acidity on the isosynthesis reaction a series of four catalysts were synthesized and tested for isosynthesis activity. These catalysts included three zirconium dioxides doped with metal oxides of decreasing acidity ($Sc_2O_3 > Y_2O_3 > Sm_2O_3$) at 9 mol% that form the fluorite crystal structure and acid-modified zirconium dioxide, which is made from treating zirconium dioxide in H_2SO_4 prior to calcination and forms a monoclinic crystal structure. The results are shown in Table 3.

The three metal oxides given above are listed in order of their cation size, which at constant ionic charge, indicates acid strength. The smaller the cation is, the more acidic it will be (*36*). Although size/acidity relationship allows us to rank the M_2O_3 oxides, another method was required to rank all the catalysts used. Many methods of measuring acidity are cited in the literature and an appropriate method was chosen that would be relevant to this study. Dehydration of 2-alcohols was used; the ratio of 1-olefin/2-olefin produced indicated basic strength (*15*). The greater the 1-olefin production, the greater the basicity of the catalyst. Results are listed in Table 4.

Zirconium dioxide treated with acids such as H_2SO_4 has been found to have no surface basic sites (*34*). Since the acid-modified zirconium dioxide was made in a manner similar to Ref. (*34*), we would expect little-to-no basic sites available on our H_2SO_4-treated

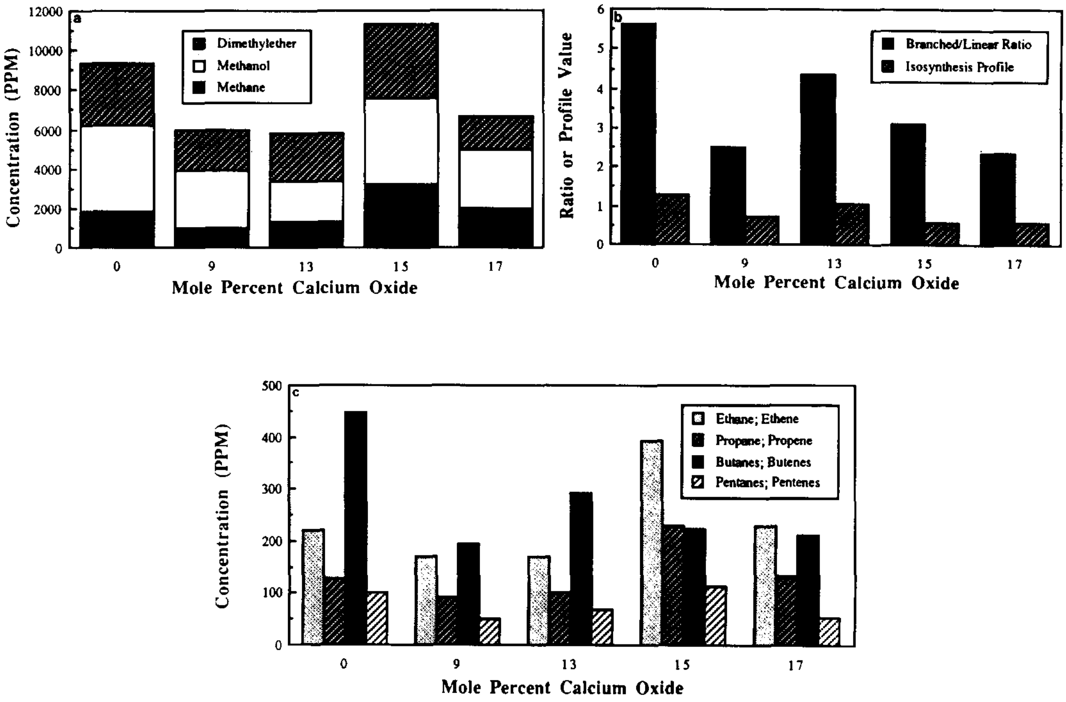

FIG. 3. Isosynthesis product formation over ZrO_2 and ZrO_2–CaO-mixed oxide catalysts. Branched/linear ratio is for C_4 and C_5 species only.

catalyst. This is because the basic hydroxyl groups have been poisoned due to replacement of the basic OH groups by the acid anions.

We have assumed in this study that the isosynthesis reaction over mixed metal oxides of zirconium dioxide reflect the activities and selectivities of synthesis gas over zirconium dioxide modified by the additive rather than the reaction over surface islands of the metal oxide additive. This assumption is supported by our XPS analysis (*19*) of the distribution of the dopants on the zirconium dioxide catalysts, by our isosynthesis results, and by the C_1 activity trends reported by Silver *et al.* (*6*). For example, the isosynthesis results for the yttria-doped zirconias did not show a continuous change from a zirconium dioxide catalyst to a yttrium oxide catalyst as more and more yttria was added. Pure yttria was 1.4 times more active for C_1–C_5 hydrocarbons and 2.7 times more active for C_2–C_5 hydrocarbons than ZrO_2 and had a branched/linear ratio and isosynthesis profile of 0.67 and 0.305, respectively. The maxima in the branched/linear ratios and isosynthesis profiles at 9.1% Y_2O_3 cannot be explained by reaction solely on Y_2O_3 sites but are associated with ZrO_2 modified by Y_2O_3 because the branched/linear ratio and isosynthesis profile were higher than the values over either pure ZrO_2 and pure Y_2O_3. The same was also true for the calcia-doped zirconias. Finally, the acid-modified zirconium dioxide was the most acidic catalyst and since no other metal oxide was present, there is no question but that the acidic properties of the modified zirconium dioxide were responsible for the isosynthesis product distribution.

The calcination temperature of pure zirconium dioxide was varied, resulting in changes in activity and selectivity. The results of various calcinations are shown in

TABLE 3

Product Distribution for Isosynthesis Reactions over Zirconium Dioxide-Mixed Metal Oxide Catalysts at 425°C, 35 atm, 1/1 CO/H_2

Catalyst	Concentration (parts per million)				
	$AZrO_2$	ZrO_2	9% Sc_2O_3	9% Y_2O_3	9% Sm_2O_3
Methane	2208	1846	3176	1588	7015
Methanol	1288	4378	2651	3490	2487
Dimethylether	2	3134	2914	1532	1940
Ethane	243	51	283	149	432
Ethene	315	169	256	228	174
Propane	319	127	60	35	68
Propene	[a]	[a]	139	96	129
2-Methylpropane	81	5	33	38	2
2-Methylpropene	545	375	678	500	84
n-Butane	14	5	20	8	11
1-Butene	70	34	123	26	20
cis-2-Butene	110	12	94	25	10
trans-2-Butene	163	11	93	27	11
1,3-Butadiene	2	5	0	0	0
2-Methylbutane	49	20	8	2	1
2-Methyl-1-butene	65	21	41	28	3
2-Methyl-2-butene	163	31	97	37	10
3-Methyl-1-butene	13	10	15	8	3
2-Methyl-1,3-butadiene	0	20	0	1	0
n-Pentane	0	0	10	2	6
1-Pentene	9	11	12	6	4
cis-2-Pentene	15	3	12	3	3
trans-2-Pentene	67	4	24	4	5
Branched/linear ratio	2.04	5.62	2.25	6.17	1.48
Isosynthesis profile	1.12	1.29	1.41	1.22	0.17

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[a] Propane and propene could not be separated and propane gives total C_3 concentration.

Fig. 4. Zirconium dioxide calcined at 700, 750, and 800°C in flowing oxygen immediately prior to the isosynthesis reaction is referred to as calcination Method A. The 700°C Method A calcined zirconium dioxide showed little change from the 600°C sample. The product activity and selectivity of the catalyst calcined at 750°C (Method A) was found to change the most from the zirconium dioxide calcined at 600°C. The catalyst calcined at 750°C (Method A) showed the largest production of C_1–C_5 hydrocarbons (two to three times that of zirconium dioxide calcined only at 600°C) with a low branched-to-linear ratio. In particular, the C_2 and C_3 hydrocarbon production increased significantly for the zirconium dioxide calcined at 750°C (Method A) over the catalyst calcined at 600°C. Also characteristic of zirconium dioxide calcined at 750°C (Method A) was a distinctive methoxide product distribution which included a large amount of methane, a relatively small amount of dimethylether, virtually no methanol, and a low branched-to-linear ratio. The zirconium dioxide Method A calcined at 800°C had a total hydrocarbon production less than the sample calcined only at 600°C. In contrast, zirconium dioxide treated at 750°C in hydrocarbon-free air and then stored at room temperature for several days before isosynthesis testing (calcination Method B) showed the characteristic selectivity of zirconium dioxide calcined and pretreated at 600°C but with

TABLE 4

Selectivity of 1-Butene from 2-Butanol Dehydration at 400°C

Catalyst	Percentage 1-Butene of all 1- and 2-butenes[a]
$AZrO_2$	18.9
9% Sc_2O_3[b]	20.7
9.1% Y_2O_3	23.3
5.0% Y_2O_3	32.7
15.0% Y_2O_3	38.1
9% Sm_2O_3	45.5
9% CaO	55.7
ZrO_2	67.4
7.0% Y_2O_3	76.0
15% CaO	78.9
17% CaO	83.6
13% CaO	88.5

[a] An equilibrium mixture would be 24% 1-butene, 30% *cis*-2-butene, and 46% *trans*-2-butene.

[b] The remainder for all catalysts was ZrO_2.

decreased activity. To see whether this calcination effect was related to the acid/base strength of the catalyst, acidic 9% Sc_2O_3 and basic 9% Sm_2O_3 were compared at 600 and 750°C calcination temperatures (calcination Method A) and the basic 9% Sm_2O_3 showed a much greater increase in C_1–C_5 hydrocarbon production than the acidic 9% Sc_2O_3.

In order to determine whether the conversion increase seen for 750°C calcination Method A was a function of the dehydration of the catalyst at exposure to high temperatures, zirconium dioxide was treated at 180°C in flowing helium saturated with water at room temperature for 10 min immediately following high-temperature pretreatment at 750°C to make certain the surface was well hydrated. Zirconium dioxide was then pretreated in flowing oxygen at 600°C for 10 min to remove excess physically adsorbed water before conducting the isosynthesis reaction again. The results showed an increase in C_1–C_5 hydrocarbon production relative to isosynthesis before rehydration, and no significant changes in methoxide product formation were found.

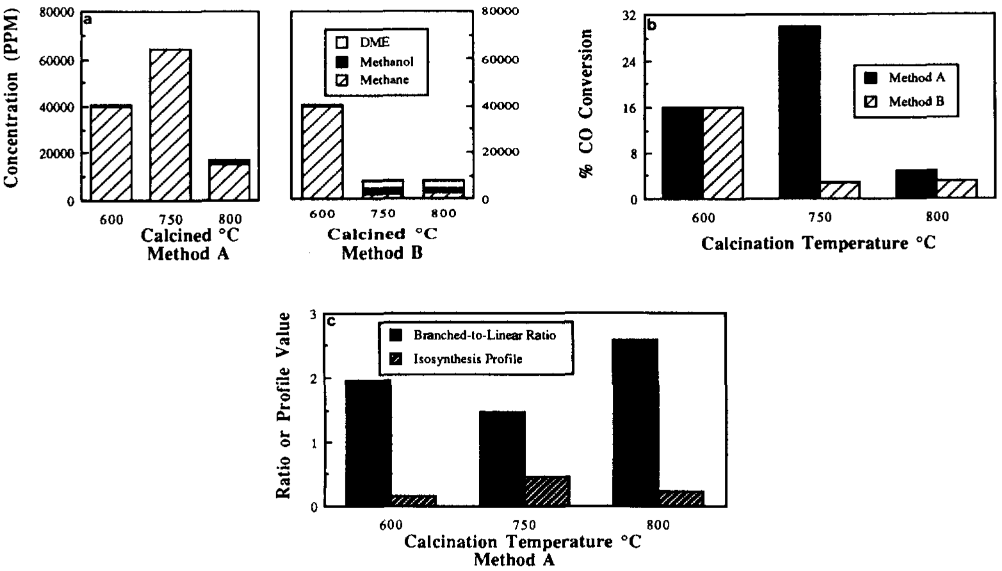

FIG. 4. Changes in the isosynthesis products following calcination at different temperatures in oxygen and then used immediately (Method A) or in hydrocarbon-free air and then stored in ambient air until use (Method B). Branched/linear ratio is for C_4 and C_5 species only.

IV. DISCUSSION

Condensation reaction. The experiments which showed the greatest influence on the condensation reaction were the acid/base and oxygen vacancy experiments. In both sets of experiments the isosynthesis profile, the relative measure of the condensation reaction, changed with changing amount of dopant. Both yttria- and calcia-doped zirconium dioxide catalysts showed a maximum isosynthesis profile and branched-to-linear ratio at the same percentage stabilization that the maximum oxygen conductivity for these oxides has been reported. Oxygen conductivity for these oxides has been associated with oxygen vacancy migration (*22, 23*). Silver *et al.* also found a maximum in atmospheric C_1 synthesis activity and surface vacancy concentration at the same 9.1 to 9.8% Y_2O_3 loading (*6*). They reasoned that this maximum was associated with the migration of vacancies to the surface. Similar reasoning applied to the results reported herein suggests that vacancy migration and their availability for reaction at the surface influenced the condensation reaction.

Oxygen vacancies have been found to be important in the formation of methoxide (*4, 6*) and were studied for their effect on the isosynthesis reaction since methoxide is also crucial to condensation. However, the enhancement of the condensation reaction from oxygen vacancy mobility does not appear to come from a large quantity of methoxide since many of the doped zirconium dioxide catalysts with lower isosynthesis profiles produced more methoxide products than the 9% Y_2O_3 and 13% CaO.

The acidity as measured by the percent 1-butene from 2-butanol dehydration (Table 4) was plotted versus the isosynthesis profile of the modified zirconia catalysts, which may be seen in Fig. 5. The lower the percent 1-butene, meaning the more acidic the modified catalyst, the higher the isosynthesis profile. Several points appear to deviate from the line created by the other points and these are numbered on Fig. 5. Point number one represents 13% CaO. All the calcia-modified zirconias were shown to be basic by the 2-butanol dehydration experiment. This is not surprising since CaO is considered a basic oxide. However, 13% CaO was known to be the calcia-modified zirconia with the greatest mobility of oxygen vacancies, and this appeared to increase significantly the isosynthesis profile above that of the other basic calcia-modified zirconias. Point number two represents 15% Y_2O_3. Fifteen mole% Y_2O_3 actually represents 30 percent Y^{3+} and 70% Zr^{4+} in the bulk and XPS showed 28% Y^{3+} at the surface (*19*). The large amount of yttria cation present may prevent the catalyst from acting as a modified zirconium dioxide catalyst. Point number three is 9% Sm_2O_3 and, as can be seen from Table 3, the samaria-modified zirconia appears to be different than the other 9% M_2O_3-modified zirconias. It is not clear why this is so, but this difference is also reflected in Fig. 5.

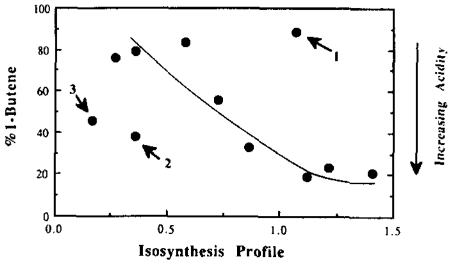

FIG. 5. Isosynthesis profile versus acidity (as measured by percentage of 1-butene formed from 2-butanol dehydration) for all modified zirconium dioxide catalysts.

The most important result from the acid–base isosynthesis experiments is that a high isosynthesis profile was associated with the more acidic catalysts (although not necessarily the largest branched-to-linear ratios). Therefore, acidic sites must enhance the condensation reaction. The amount of C_1 produced is large for the catalysts with the lowest isosynthesis profile and smallest for those with the higher profiles. The branched-to-linear ratio does not, however, follow any pattern and, unlike the yttria- and calcia-doped catalysts, cannot be correlated to the isosynthesis profile. The basic catalyst, 9% Sm_2O_3, did not make significantly less C_2 and C_3 hydrocarbons than the other acid/base catalysts; however, this basic catalyst had a low isosynthesis profile and did not appear to be able to sustain as much condensation as the more acidic catalysts.

Figure 1 indicates that enhancement of the condensation reaction must come from either the stabilization of the enolate (structures II and III) or an increase in the reactivity of the methoxide. The acidic surface appears to enhance the condensation reaction and this could be from either the stabilization of the enolate, which we favor, or activation of the methoxide. The more acidic surface may result in a more positively charged, and therefore, more reactive methoxide. However, if an increase in the surface acidity was affecting the methoxide, the Zr–O bond of the methoxide would be strengthened and the consequential weakening of the O–C bond of the methoxide would cause its greater reactivity. If this were happening, the methane/methanol production ratio would also reflect this relative change in bond strength. A change in methane/methanol production ratio was not observed. In addition, there was not a correlation between condensation, as measured by the isosynthesis profile, and a methane/methanol production ratio. The most likely possibility for the enhancement of the condensation reaction is that the Lewis acid sites (electron acceptors), such as on $AZrO_2$ are capable of stabilizing the enolate, an electron-rich species.

Oxygen vacancy sites may also be considered electron acceptor sites. The oxygen vacancies in the bulk of yttria-doped zirconium dioxide have been proposed to occur most often next to a Zr^{4+} cation (*26*). If the close proximity between Zr^{4+} and an oxygen vacancy were also true on the surface, the oxygen vacancy would have a localized effect of making the Zr^{4+} cation more electron accepting. The doped zirconium dioxides with the greatest oxygen mobility may be best able to make available oxygen vacancies, and therefore effective electron accepting sites, at the surface where they are involved in the condensation reaction.

Our work supports the proposal from Mazanec that a second reaction, condensation, is responsible for deviations from Schulz–Flory product distributions for isosynthesis reactions. However, unlike Mazanec's proposed scheme, we found that condensation contributed more to the production of C_4's rather than C_3's as can be seen by the step increase in C_4's over C_3's and in the lower level of incorporation of labeled methanol into C_3 products over C_4 products (*18*, *19*). The results in this study supporting the stabilization of the enolate by acidic sites may appear to contradict what has been reported about the basic catalyzed condensation reaction of higher branched alcohol synthesis over alkali promoted Cu/ZnO catalysts. Although the isosynthesis reaction over zirconium dioxide and the higher alcohol formation over Cu/ZnO catalysts both lead to branched products, they represent two different types of reactions taking place over dissimilar catalysts. Alkali promoters added to Cu/ZnO catalysts have long been known to increase the production of higher alcohols, particularly branched alcohols. However, the use of alkali promoters over zirconium dioxide was found to decrease the formation of products from the condensation reaction (*19*).

Branched-to-linear ratio. As can be seen from Fig. 1, branched products may be formed from both condensation and CO insertion. The branched-to-linear ratio is not necessarily an indicator of either reaction and is actually the result of a complicated possibility of reactions. Therefore, insight into the relative rates of insertion versus condensation or into the relative stability of intermediates II–V is not possible on the basis of the branched-to-linear product ratio.

CO insertion reaction. The only surface modification leading to a significant increase in the CO insertion reaction is seen in the change of calcination temperature from 600 to 750°C for calcination Method A. The sharp increase in C_2 and C_3 products seen with the change in calcination temperature can only be caused by the CO insertion reaction since the condensation reaction does not lead to C_2 products and does not appear to be significant for C_3 products. The isosynthesis profile also increased with increased calcination temperature (calcination Method A) indicating an increase in the condensation reaction as well.

The maximum activity for zirconium dioxide calcined (Method A) at 750°C corresponds with pretreatment temperature where the maximum activity was found in the study of 1-butene isomerization over zirconium dioxide by Nakano *et al.* (*32*). The number of strongly basic sites was found to be at a maximum at this point. Acidic sites were also found to be stronger on zirconium dioxide pretreated at 700°C than zirconium dioxide pretreated at 500°C.

Calcination temperatures are the same for both calcination Methods A and B. However, since Method B catalysts were exposed to the atmosphere for some time before isosynthesis testing, the effect of atmospheric variables, CO_2 and water, were considered. Adsorbed CO_2 forms carbonates on the zirconium dioxide surface but these are known to desorb at 600°C (*1, 2*) and all catalysts were pretreated for at least 10 min at 600°C in oxygen before testing to ensure the desorption of all carbonates. High-temperature calcination was suspected of dehydrating the surface more effectively than pretreatment at 600°C. Additional evidence of dehydration came from the change in C_1 products with high, Method A, calcination temperature. There was a large increase in methane, methanol was no longer produced, and some dimethylether formed after Method A calcination temperature of 750°C. This change in C_1 products would indicate a dehydration of the surface since water is necessary for the formation of methanol and lack of water leads to methane formation (*4*). However, rehydration of the catalyst after 750°C calcination Method A served only to increase C_1–C_5 hydrocarbon production by increasing CO insertion (activity increased but isosynthesis profile did not) and did not restore methanol formation. The decrease in activity of the zirconium dioxide calcined at 800°C (Method A) may be due to the dehydroxylation of the zirconium dioxide surface which has been reported to occur at temperatures greater than 750°C (*36*). The zirconium dioxide catalyst calcined (Method B) at 800°C may have had time to rehydroxylate the surface before isosynthesis testing by exposure to the ambient atmosphere allowing it to react similarly to the catalysts calcined at 750°C (Method B).

The only measured difference found between catalysts calcined by Method A versus Method B, besides activity, was the X-ray diffraction patterns of the catalysts. The catalysts calcined by Method B at 750 and 800°C were 100% monoclinic; the sample calcined at 750°C Method A was 95.5% monoclinic/4.5% tetragonal and 800°C Method A was 95.2% monoclinic/4.8% tetragonal. However, for all batches of zirconium dioxide and for all calcination regimens there was no correlation between phase and the quantity of C_2 and C_3 production (indication of CO insertion activity) or between phase and the isosynthesis profile (indication of condensation activity). Therefore, it appears that phase has little effect on the two chain growth reactions.

Calcination of acidic 9% Sc_2O_3 and basic 9% Sm_2O_3 at 750°C by Method A showed that the basic catalyst increased significantly more in activity by this modification, particularly in C_2 and C_3 production, than by the acidic catalyst. Calcination Method A at 750°C seems to enhance the CO insertion reaction more on the more basic catalysts.

In summary, the surface change from calcination Method A at 750°C that effects the rate of the CO insertion reaction and slightly increases the isosynthesis profile is (1) not a dehydration phenomena since rehydration only increased the CO insertion rate and dehydroxylation decreased the rate and (2) not a bulk phase change since the bulk phase of zirconium dioxide does not appear to have a significant effect on the isosynthesis chain growth reactions. The activity change with calcination at 750°C (Method A) suggests that the CO insertion reaction is enhanced by basic sites and the strong basic sites appear to be enhanced by calcination at 750°C (Method A). Enhancement of basic sites by high-temperature treatment is also seen in Ref. (*32*) and by the more significant increase in activity for the basic catalyst, 9% Sm_2O_3, calcined at 750°C (Method A) than that for the acidic catalyst, 9% Sc_2O_3. The contribution of basic sites toward increasing activity by enhancing the CO insertion reaction explains why thorium dioxide, which is considered a basic metal oxide (*17, 36*), is a more active isosynthesis catalyst than zirconium dioxide.

V. CONCLUSIONS

The condensation reaction is enhanced by strong electron accepting sites such as oxygen vacancies and Lewis acid sites. The CO insertion reaction is enhanced by basic sites which are activated by high temperature treatment to the catalyst immediately before the isosynthesis reaction. The basic sites that enhance CO insertion are further enhanced by a well-hydrated catalyst and are not deactivated by water. Basic sites activated by high-temperature pretreatment enhance the CO insertion reaction more than acidic sites treated in the same manner. Therefore, an isosynthesis catalyst needs to be an acid–base bifunctional catalyst with strong acid and base sites. The balance between the strength and quantity of the acid and base sites are what govern the selectivity of the isosynthesis reaction.

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REFERENCES

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

2. He, M-Y., and Ekerdt, J. G., *J. Catal.* **87,** 238 (1984).

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

4. Jackson, N. B., and Ekerdt, J. G., *J. Catal.* **101,** 90 (1986).

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

6. Silver, R. G., Hou, C. J., and Ekerdt, J. G., *J. Catal.* **118,** 400 (1989).

7. Silver, R. G., Jackson, N. B., and Ekerdt, J. G. *in* "Catalytic Activation of Carbon Dioxide," (W. M. Ayers, Ed.), ACS Symposium Series 363, American Chemical Society, Washington, DC, 1988.

8. Maehashi, T., Maruya, K., Domen, K., Aika, K., and Onishi, T., *Chem. Lett.* **747** (1984).

9. Kieffer, R., Cherry, G., and El Bacha, R., *C_1 Mol. Chem.* **2,** 11 (1987).

10. Maruya, K., Maehashi, T., Haraoka, T., Narui, S., Asakawa, Y., Domen, K., and Onishi, T., *Bull. Chem. Soc. Japan,* **61,** 667 (1988).

11. Abe, H., Maruya, K., Domen, K., and Onishi, T., *Chem. Lett.* **1875** (1984).

12. Kondo, J., Abe, H., Sakata, Y., Maruya, K., Domen, K., and Onishi, T., *J. Chem. Soc., Faraday Trans. 1* **84,** 511 (1988).

13. Mazanec, T. J., *J. Catal.* **98,** 115 (1986).

14. Sonnenberger, D. C., Mintz, E. A., and Marks, T. J., *J. Amer. Chem. Soc.* **106,** 3484 (1984).

15. Davis, B. H., *Ads. Catal. Oxide Surf.* **309** (1985).

16. Lundeen, A. J. and Van Hoozer, R., *J. Org. Chem.* **32,** 3386 (1967).

17. Canesson, P. and Blanchard, M., *J. Catal.* **42,** 205 (1976).

18. Tseng, S. C., unpublished data, Department of Chemical Engineering, University of Texas, Austin.

19. Jackson, N. B., Ph.D. thesis, Department of Chemical Engineering, University of Texas, Austin, 1990.

20. Tseng, S. C., Ph.D. thesis, Department of Chemical Engineering, University of Texas, Austin, 1987.

21. Vedage, G. A., Himelfarb, P. B., Simmons, G. W. and Klier, K., *in* "Solid State Chemistry in Catalysis" (R. K. Grasselli and J. F. Brazdil, Eds.), p. 295–312, ACS Symposium Series 279, American Chemical Society, Washington, DC, 1985.

22. Etsell, T. H., and Flengas, S. N., *Chem. Rev.* **70,** 339 (1970); and references therein.
23. Heyne, L., *in* "Mass Transport in Oxides," Vol. 296, p. 149, National Bureau of Standards Special Publication, 1968.
24. Kingerly, W. D., Papis, J., Doty, M. E., and Hill, D. C., *J. Amer. Ceram. Soc.* **42,** 393 (1959).
25. Despert-Ghys, J., Faucher, M., and Caro, P., *J. Solid State Chem.* **84,** 179 (1984).
26. Catlow, C. R. A., Chadwick, A. V., Greaves, G. N., and Moroney, L. M., *J. Amer. Ceram. Soc.* **69,** 272 (1986).
27. McCullough, J. D., and Trueblood, K. N., *Acta Crystallogr.* **12,** 507 (1959).
28. Evans, P. A., Stevens, R., and Binner, J. G. P., *Trans. J. Br. Ceram. Soc.* **83,** 39 (1984).
29. Scott, H. G., *J. Mater. Sci.* **10,** 1527 (1975).
30. Paterson, A., and Stevens, R., *J. Mater. Res.* **1,** 295 (1986).
31. Strickler, D. W. and Carlson, W. G., *J. Amer. Ceram. Soc.* **48,** 286 (1965).
32. Nakano, Y., Iizuka, T., Hattori, H., Tanabe, K., *J. Catal.* 57, 1 (1979).
33. Nitta, M., Sakoh, H., and Aomura, K., *Appl. Catal.* **10,** 215 (1984).
34. Walvekar, S. P., Sriniwasan, T. N., Bhargawa, P., Nanjegowda, N. M., and Nagaraju, N., *in* "Advances in Catalysis Science and Technology," Wiley Eastern Ltd., New Delhi, 1985.
35. Davis, B. H., *J. Catal* **58,** 493 (1979).
36. Tret'yakov, N. E., Pozdnyakov, D. VB., Oranskaya, O. M., and Filimonov, V. N., *Russ. J. Phys. Chem.* **44,** 596 (1970).