JOURNAL OF CATALYSIS **126**, 46–56 (1990)

Isotope Studies of the Effect of Acid Sites on the Reactions of C_3 Intermediates during Isosynthesis over Zirconium Dioxide and Modified Zirconium Dioxide

NANCY B. JACKSON AND JOHN G. EKERDT

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

Received November 15, 1989; revised March 19, 1990

CO hydrogenation reactions over zirconium dioxide at 425°C and 35 atm proceeds by two chain growth steps to C_4 products, CO insertion into aldehydic Zr–C bonds, and condensation between methoxide and η^3-enolates. Carbon-13-labeled acetone and methanol were co-fed with CO/H_2 to study the effect of surface acid and base characteristics on the C_3 intermediates and their reactions leading to C_4 hydrocarbon products. Studies were conducted over zirconium dioxide, H_2SO_4 modified zirconium dioxide, 9% Sc_2O_3–ZrO_2, 9% Y_2O_3–ZrO_2, and 9% Sm_2O_3–ZrO_2. Branched C_3 intermediates were more likely than linear C_3 intermediates to form on acidic catalysts. Lewis acid sites enhanced the condensation reaction involving a reaction between an η^3-enolate and a methoxide. The more acidic the catalyst, the greater the percentage of C_4 products. However, the most acidic catalysts did not necessarily have the highest branched-to-linear ratios. The importance of enolate stabilization and of the condensation reaction on the isosynthesis reaction are discussed.

I. INTRODUCTION

Isosynthesis, the synthesis gas reaction over certain metal oxides such as ThO_2 and ZrO_2, is unique for its selectivity toward branched hydrocarbons, particularly branched C_4 hydrocarbon products. This laboratory has studied isosynthesis over zirconium dioxide and has proposed two chain growth reactions found in isosynthesis (*1*) and has suggested (*2*) catalyst surface characteristics required for this reaction. These two reactions are the CO insertion reaction and a condensation reaction. The insertion reaction involves insertion of CO into the Zr–C bond of a surface aldehydic intermediate. The condensation reaction takes place between an η^3-enolate and a methoxide species. The condensation reaction contributes primarily to C_4 and C_{4+} products which explains the characteristic increase in C_4 products over C_3 products for the isosynthesis reaction. (Some condensation reaction contributes to C_3 formation but is less significant than for C_4 synthesis (*2*).) The relative importance of the condensation reaction can be gauged from the size of the isosynthesis profile, a number defined as $C_4/(C_2 + C_3)$ (*2*).

This study focuses on the effects of surface acid/base characteristics on C_3 intermediates and their reactions leading to C_4 hydrocarbon production over zirconium dioxide and modified zirconium dioxides. Figure 1 shows the C_3 intermediates, their possible reactions and their C_4 products (*1–3*). There are two isomers of the η^3–C_3-enolate, branched I and linear II, and both types can undergo condensation with a methoxide to form a C_4 species. Condensation is a β-addition reaction; therefore, condensation with a branched enolate forms a linear C_4 product and condensation with a linear enolate forms a branched C_4 product. There are also two isomers, branched and linear, which are likely in equilibrium with the enolates and which undergo CO insertion: the branched adsorbed ketone III and the linear adsorbed

0021-9517/90 $3.00

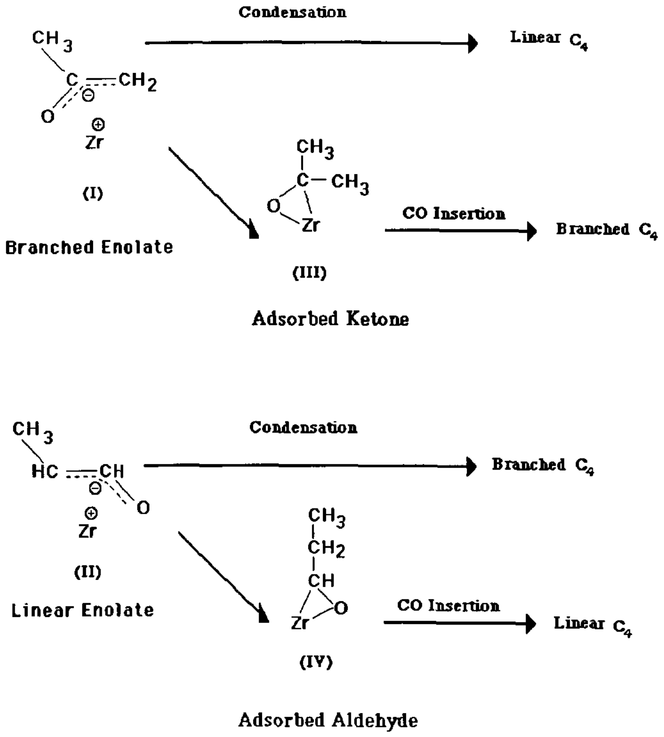

FIG. 1. Four C_3 intermediates and the two possible reactions that result in four different routes to C_4 synthesis over zirconium dioxide.

aldehyde IV. CO insertion is an α-addition reaction. Therefore, CO insertion into a linear adsorbed aldehyde leads to a linear C_4 product; CO insertion into a branched adsorbed ketone leads to a branched C_4 product. Following the CO insertion or condensation reactions, a new set of C_4 enolates and aldehydes/ketones are formed which can undergo further reaction to C_5 and C_{5+} products or can desorb to the C_4 hydrocarbon products shown in Fig. 1 (*1*). The reactions looked at in this study are the ones that lead to C_4's only.

Several studies have been done on the surface properties required of isosynthesis catalysts (*2–5*). Earlier work in this laboratory (*2*) reported that on zirconium dioxide and mixed metal oxides of zirconium dioxide at 425°C and 35 atm, acid sites promoted the condensation reaction and basic sites were important to the CO insertion reaction. Acidic zirconium dioxide catalysts such as ZrO_2 modified with H_2SO_4 and 9% Sc_2O_3 in ZrO_2 showed high isosynthesis profiles, which implies a high rate for the condensation reaction, but did not necessarily have a large percentage of 2-methylpropene formation. Therefore, acidic sites were shown to enhance the condensation reaction but not necessarily 2-methylpropene production. It appears that acid sites might preferentially enhance the branched enolate. A preference for the branched enolate has been proposed as being a characteristic of the isosynthesis catalyst; however, basic sites were credited for causing this preference (*3*). Since both branched and linear enolates come from the same C_2 precursor, the relative stability of the two enolates will effect the branched-to-linear ratio of the products. The stability of the enolate versus the aldehyde/ketone will also have an effect on the product distribution. The more stable the enolate, the longer it will exist, and therefore, the more likely condensation is to take place versus CO insertion. Lewis acid sites have been suggested to promote the condensation reaction by stabilization of the enolate (*2*).

Maruya *et al.* (*4*) studied the selectivity of synthesis gas over zirconium dioxide and mixed metal oxides of zirconium dioxide in a gas-recirculating glass reaction system at one atmosphere. They suggested that there were two active sites on zirconium dioxide, one that promoted methane formation and one that led to C_4 hydrocarbon production since there was an inverse relationship between C_1 formation and C_4 formation for all their mixed metal oxides. They found that the more electronegative the oxide additive to zirconium dioxide the more it promoted methane formation over C_4 formation. Sodium hydroxide, the least electronegative oxide mixed with zirconium dioxide in their study, was the most selective catalyst for C_4 hydrocarbon formation, especially 2-methylpropene, as a percentage of all C_1–C_6 hydrocarbons. This led them to suggest that the importance of the basic character of the active site for 2-methylpropene formation.

A reaction which resembles the isosynthesis condensation reaction is the synthesis gas reaction over the Cu/ZnO methanol catalyst promoted with alkali. Klier and coworkers (*5, 6*) have studied the synthesis of higher alcohols (branched C_4 alcohols are the main C_4 products) that are made over Cu/ZnO doped with alkali hydroxide. A condensation type reaction with an enolate and a β-ketoalkoxide intermediate was proposed by Klier (*5, 6*) who found that the synthesis of higher alcohols was promoted by alkali via the condensation reaction. In particular, the ability of a promoter cation to stabilize the enolate and β-ketoalkoxide structure participating in this mechanism (*6*) was responsible for the alkali promotion effect. The alkali promotion effects of Cs, Rb, K, Na, and Li were tested and CsOH-doped catalysts showed the most significant effects followed by Rb > K > Na > Li. This indicated that a base-catalyzed reaction was being promoted (*5*). The more basic the alkali hydroxide, the larger the cation is. The enolate, which is highly carbenic in nature, may be stabilized by the large alkali cation (*5, 6*). Other reactions involving carbanions are thought to be enhanced by alkali-containing catalysts (*7*).

To determine the effects of surface acidity on the isosynthesis reaction, zirconium dioxide was modified by the addition of other metal oxides or acids which influenced the acidity of the zirconium dioxide. The modified zirconium dioxides used are listed in order of increasing acidity: 9% Sm_2O_3 < 9% Y_2O_3 < 9% Sc_2O_3 < H_2SO_4 acid-modified ZrO_2. For a discussion on the structure and surface nature of these catalysts, see Ref. (*2*). To study the effect acidity/basicity has on the relative rates of the two different reactions and four possible routes (Fig. 1) to C_4 synthesis, acetone-2-^{13}C was introduced into the reactant stream and the labeled C_4 products were monitored. According to the mechanistic schemes developed in Ref. (*1*), adsorbed acetone is capable of either converting to a branched enolate and then condensing with a methoxide to form a linear C_4 or undergoing CO insertion to form a branched C_4 product. Therefore, the ratio of branched-to-linear-labeled C_4 products should indicate the rate of CO insertion versus condensation into a branched C_3 intermediate.

In addition, experiments adding ^{13}C-methanol to the synthesis gas reactant stream were conducted. Methanol is known to adsorb on zirconium dioxide as a methoxide (*8*). The relative rates of methoxide condensation with branched versus linear enolates were observed by the monitoring of C_4 products labeled with one carbon-13.

II. METHODS

Apparatus. The reactor was 28 cm long and made out of 0.533-cm i.d. 316 stainless steel tubing. A new reactor was used for every experiment to avoid possible contamination. Gases were heated to 150°C prior to entering the reactor. Isotopic compounds were introduced into the CO/H_2 reactant stream using a HPLC syringe pump, Isco Model μLC-500. The pump outlet was heated to 150°C.

Analysis was completed with a Hewlett–Packard 5890A gas chromatograph (GC) using both a flame ionization detector (FID) and a Hewlett–Packard 59970 mass spectrometer detector (MSD). Reactor effluent was analyzed by direct injection into a BP-1 megabore capillary column (Scientific Glass and Engineering dimethyl siloxane bonded phase, 5.0-μm thick film, aluminum clad, 25 m × 0.53 mm i.d.) from a 1-ml sample valve filled directly from reactor effluent. The BP-1 column was used to analyze gas composition with an FID. This column was able to separate all species except 2-methylpropene from 1-butene and *n*-butane from methanol. Isotopic distribution of C_4 products was determined with the HP 59970 MSD by gas tight-syringe injection 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). Other compounds were also monitored including CO, CO_2, dimethylether, C_3's, and C_5's.

The picric acid column was able to separate 1-butene from 2-methylpropene and *n*-butane from methanol. Integration of the chromatogram generated by the MSD allowed quantitative determination of 2-methylpropene and 1-butene that could not be separated with the BP-1 column. The C_4 products that were monitored included 1-butene, *cis*-2-butene, *trans*-2-butene, 2-methylpropane, and 2-methylpropene. Oxygenated C_4's such as isobutyraldehyde and 2-methylpropanol were not found in measurable quantities.

Isotopic distributions were computed with a regression analysis program that compared the mass fragmentation pattern for a GC/MS peak to the pattern observed for the same peak in the absence of a ^{13}C feed additive. The percentage of ^{13}C in a molecule but not the location of the isotopic carbon could be determined. The accuracy of this method was about 1% and isotopic percentages below this level may not signify ^{13}C incorporation.

Materials. All catalysts were made as described in Ref. (*2*) and were calcined for 4 h in hydrocarbon-free air at 600°C before use. Acetone-2-^{13}C was purchased from MSD Isotopes and was 90 atom percent ^{13}C. The acetone-2-^{13}C was diluted with acetone-1,2,3-^{12}C in an approximately 50/50 mixture in order to ensure there was enough acetone-2-^{13}C for the experiments performed.

^{13}C-Methanol was purchased from Isotec, Inc. and the first 5 ml was 99.4 atom percent ^{13}C. ^{13}C-Methanol was initially used as a 50/50 mixture with ^{12}C-methanol; however, the difficulty in detecting ^{13}C-containing hydrocarbons led to using 99.5 atom percent ^{13}C (also from Isotec) without dilution. This did not change the detection of ^{13}C-containing hydrocarbons appreciably.

Procedure. Each experiment used 2 g of catalyst which was pretreated at 600°C in oxygen for 10 min. The reactor was flushed with helium and then a premixed 50/50 mixture of CO/H_2 was allowed to flow over the catalysts at 100 sccm and 500 psi at 425°C. The isosynthesis reaction was run for 2 h before any isotopic feed was introduced. Acetone was introduced initially at very slow feed rates (0.05–0.10 μl/min) and was then increased incrementally. The C_3 to C_5 products were seen to rise slowly with increasing acetone addition. The results were the same regardless of whether the acetone was added in increasing or decreasing increments. There was no hysteresis effect observed.

^{13}C-Methanol experiments were conducted similarly. However, except for the experiments with 9% Sc_2O_3 and $AZrO_2$, which are discussed below, the methanol experiments had very little effect on the product distribution of the isosynthesis reaction.

III. RESULTS

To determine the relative rates for the CO insertion reaction versus the condensation

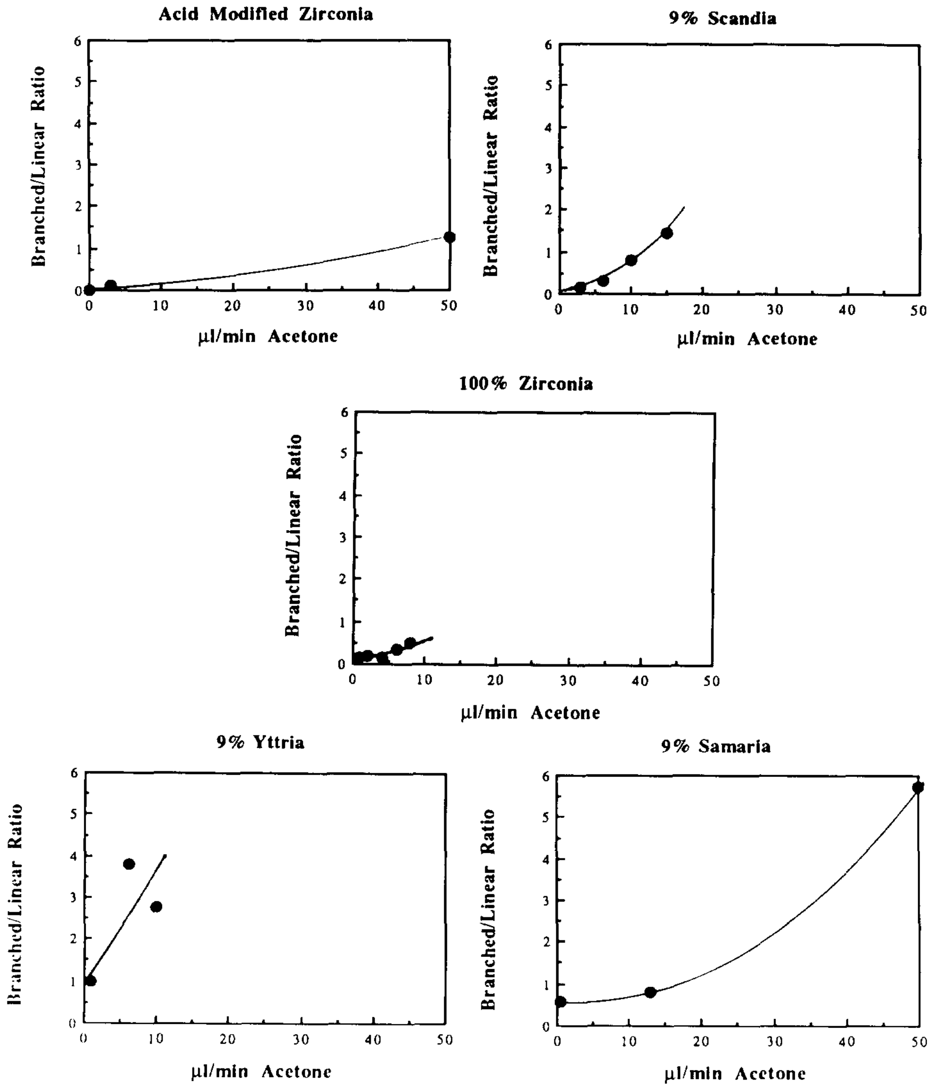

FIG. 2. Branched-to-linear ratio of C_4 products incorporating one carbon-13 versus flow rate of acetone-2-^{13}C.

reaction with branched C_3 intermediates over zirconium dioxide and zirconium dioxide-mixed metal oxides of varying acidity, acetone-2-^{13}C was introduced into the reactant stream and the labeled C_4 products were monitored. The total amount of C_4 hydrocarbon products was calculated and the percentage of each of the C_4 products that was labeled with one carbon-13 was multiplied by the total amount of that product to give the total amount of labeled material. Branched-to-linear ratios of labeled C_4 products were determined at each flow rate and are shown in Fig. 2. The branched-to-linear ratio was extrapolated to zero feed rate and the intercept value represents what the branched-to-linear ratio for products originating from the branched enolate would be without acetone present in the feed. Since branched C_4-labeled products are made by CO insertion into a ketone and linear C_4-labeled products are made by condensation

TABLE 1

Condensation versus CO Insertion for Adsorbed Acetone-2-^{13}C

Catalyst	Condensation/CO insertion ratio
AZrO$_2$	50.2
9% Sc$_2$O$_3$	10.0
ZrO$_2$	8.3
9% Sm$_2$O$_3$	1.69
9% Y$_2$O$_3$	1.0

with a branched enolate, the reciprocal value of the intercept is the ratio of condensation versus CO insertion rates. The ratio of condensation versus CO insertion rate is tabulated for each catalyst in Table 1.

At large flow rates of acetone, propane, and propene production products were found labeled with one carbon-13 and total C$_3$ production increased significantly. Since C$_6$ products were not monitored, the possibility of a self-condensation reaction of acetone was not investigated.

^{13}C-Methanol was introduced into the reactant stream at very small flow rates, 0.05 μl/min, and was increased until it was incorporated into the C$_4$ products but before ^{13}C-methanol was oxidized, and ^{13}CO and ^{13}CO$_2$ could be seen in the effluent stream. The fraction of each C$_4$ hydrocarbon with labeled carbon was multiplied by the quantity of that C$_4$ product to give the actual concentration of labeled C$_4$ products. The branched-to-linear ratios of these labeled products were calculated and are listed in Table 2. It was difficult to see ^{13}C incorporation into the C$_4$'s without adding so much methanol that it began to oxidize to CO and CO$_2$. The methanol addition could not be extrapolated to zero feed rate as the acetone experiments were because only about one point could be taken before significant ^{13}CO and ^{13}CO$_2$ were seen. Therefore, the branched-to-linear ratio of ^{13}C-incorporated C$_4$ products represented a value as close to zero feed rate of methanol as could be obtained. Before methanol was added to the reactant stream, the branched-to-linear ratio of all C$_4$'s and the concentration of C$_4$ products was noted and is recorded in Table 3. Due to the low activity of the 9% Sm$_2$O$_3$, particularly the low production of C$_4$ products, methanol incorporation for this catalyst was not obtained.

Introduction of the oxygenates was done at the minimum level possible for incorporation and detection, without perturbing the system. However, some catalysts were more sensitive to oxygenate addition than others. The addition of only 0.05 μl/min of methanol to the isosynthesis reaction over acid-modified zirconium dioxide caused a significant change in the selectivity of that reaction. The isosynthesis profile dropped to one-fifth its original value and the branched-to-linear ratio doubled. The C$_4$ and C$_5$ hydrocarbon production was cut by about one-half. The 9% Sc$_2$O$_3$ catalyst also changed upon the addition of 0.5 μl/min methanol. The branched-to-linear ratio dropped and the C$_4$ and C$_5$ hydrocarbon production increased. The other catalysts did not change activity or selectivity significantly until very high (15.0 μl/min and above) flow rates of acetone or methanol were reached.

Branched-to-linear ratios and isosynthesis profile values were lower for this study than they were for previous work (*1*, *2*). For example, zirconium dioxide has been reported to have a branched-to-linear ratio as high as 3.0 (*1*) and 5.6 (*2*). The reason for this change is not fully understood.

TABLE 2

Incorporation of ^{13}C Methanol into C$_4$'s

Catalyst	Percentage of branched C$_4$'s incorporating one ^{13}C	Branched/linear ratio of C$_4$'s incorporating one ^{13}C
AZrO$_2$	18.5	0.23
9% Sc$_2$O$_3$	31.3	0.46
ZrO$_2$	32.4	0.48
9% Y$_2$O$_3$	63.0	1.70

TABLE 3

Isosynthesis Data—No Oxygen Additives

Catalyst	Concentration (parts per million)			
	ZrO_2	$AZrO_2$	9% Sc_2O_3	9% Y_2O_3
Methane	24460	280	8194	45720
Methanol	9480	295	362	12420
Dimethylether	1080	0	1330	430
Ethane	3160	17	962	9810
Ethene	3330	60	[a]	[a]
Propane and propene[b]	3650	40	380	6120
2-Methylpropane	165	19	3	99
2-Methylpropene	191	255	63	326
n-Butane	1210	69	154	1550
1-Butene	881	69	49	398
cis-2-Butene	165	87	21	442
trans-2-Butene	242	123	54	569
1,3-Butadiene				
2-Methylbutane	109	9	6	128
2-Methyl-1-butene	0	32	0	0
2-Methyl-2-butene	145	93	12	223
3-Methyl-1-butene	31	6	6	23
2-Methyl-1,3-butadiene				
n-Pentane	519	46	25	765
1-Pentene	80	9	6	81
cis-2-Pentene	39	15	4	142
trans-2-Pentene	80	40	7	268
Branched/linear ratio	0.249	0.951	0.304	0.236
Isosynthesis profile	0.219	5.14	0.237	0.161
C_4 branched/linear ratio	0.191	0.839	0.261	0.199

[a] Ethane and ethene could not be separated. Total C_2 concentration is listed under ethane.

[b] Propane and propene could not be separated. This represents total C_3 concentration.

However, by looking at Table 3, it can be seen that there are changes in the product distribution for ZrO_2, 9% Y_2O_3, and 9% Sc_2O_3 isosynthesis catalysts from Ref. (*2*) other than just in the branched-to-linear ratios and isosynthesis profile values. For ZrO_2, 9% Sc_2O_3, and 9% Y_2O_3, the C_2 and C_3 production increased, implying an increase in the CO insertion reaction. For ZrO_2 and 9% Y_2O_3 the overall activity increased and the product distribution appeared to be what would be expected from a reaction with a pretreatment temperature of about 750°C rather than 600°C (*2*). An additional thermocouple was applied to the reactor at several locations to monitor for a localized high temperature spot, but none were found. The experiments reported here used a different CO/H_2 source, different reactor heater, and no carbonyl trap. Analysis of the gas entering the reactor revealed 200 ppm of O_2. The CO/H_2 entering the reactor in previous work (*2*) was not analyzed for O_2. For three catalysts, ZrO_2, acid-modified ZrO_2, and 9% Y_2O_3, the amount of C_4 products, including 2-methylpropene, either stayed the same or increased. Whatever caused the change in product distribution did not necessarily change the amount of condensation reaction taking place, but probably increased the CO insertion reaction.

IV. DISCUSSION

The labeled acetone experiments measure the rate of CO insertion versus condensation for products originating with branched C_3 ketone or enolate, respectively. This rate may not be identical to the overall condensation versus CO insertion rate since it is only measuring the reaction of the branched C_3 intermediates (what forms from adsorbed acetone) but it may give an indication of the relative ratio of the overall condensation versus CO insertion rates on these catalysts. It may be noted that the most acidic catalysts have the higher condensation/CO insertion rate (Table 1) which verifies the proposition that acid sites enhance the condensation reaction (*2*). The enolate is an electron rich species and acidic sites, i.e., electron acceptor sites, are likely to be best able to stabilize these species to give them enough time to react in the condensation reaction.

Since methanol forms methoxide on the surface of zirconium dioxide, the labeled methanol experiments indicate the ratio of branched-to-linear C_4 products that were formed from the condensation reaction. Table 2 shows that the more acidic catalyst has the lowest branched-to-linear overall hydrocarbon production rate indicating that on the acidic catalysts, condensation occurs more with the branched enolate than with the linear enolate. This result is consistent with conclusions reached in a previous publication that were based on selectivity patterns (*2*).

From the methanol and acetone experiments four different pieces of information are known about C_4 formation over each catalyst: (1) the concentration of C_4 species; (2) the branched-to-linear ratio of all the C_4 products; (3) the CO insertion versus condensation rate for the branched C_3 intermediates originating from acetone-2-^{13}C; and (4) the relative condensation rates between the branched and linear enolates ($^{13}CH_3OH$). With these four values, the percentages of each of the four intermediates and their reactions leading to C_4 products can be calculated, assuming each to have the same reactivity. The following equation and relations may be written:

$C_L + C_B + I_B + I_L$ = Concentration of C_4 species

C_B/C_L = Branched C_4 products containing one ^{13}C from methanol/linear C_4 products containing one ^{13}C from methanol (at the lowest possible feed rate)

$(C_B + I_B)/(C_L + I_L)$ = Branched/linear ratio of all C_4 species

I_B/C_L = Branched/linear ratio of acetone-2-^{13}C incorporating C_4's (extrapolated to zero feed rate),

where

C_B, branched C_4 product produced by condensation with a linear enolate

C_L, linear C_4 product produced by condensation with a branched enolate

I_B, branched C_4 product produced by CO insertion with a ketone

I_L, linear C_4 product produced by CO insertion with an aldehyde.

The data for these equations are listed in Tables 1–3 and the calculated results are listed in Table 4.

Several assumptions have gone into these calculations, including (1) all C_3 intermediates are assumed to have the same reactivity, (2) all reacted C_3 intermediates are assumed to have the same fraction of those that desorb as C_4 versus those that react further to C_{5+}, (3) the methanol additive data are assumed to be the equivalent of zero feed rate, and (4) the zero feed condition was equivalent over a given catalyst for the three different loadings and feed conditions. The values in Table 4 are intended to

TABLE 4

Calculated Percentage of Intermediates Involved in C_4 Synthesis

Product	Reaction	Intermediate	Percentage of reaction/ intermediate present Catalyst		
			9% Sc_2O_3	ZrO_2	9% Y_2O_3
Branched C_4 (C_L)	Condensation	Linear enolate	17	13	6
Linear C_4 (C_B)	Condensation	Branched enolate	38	27	6
Branched C_4 (I_B)	CO insertion	Ketone	4	3	11
Linear C_4 (I_L)	CO insertion	Aldehyde	41	57	77
Branched/linear enolate			2.2	2.1	0.60
Condensation/CO insertion			1.2	0.67	0.19

be relative, not absolute, values which show a trend that is consistent with all other data.

The results in Table 4 show that the more acidic the catalyst, the more likely condensation is to take place. This result agrees with the work of Vedage *et al.* (*5*) in that the stabilization of the enolate is what enhances the condensation reaction. However, it varies from work over Cu/ZnO catalysts (*5*, *6*) in that over zirconium dioxide, acidic sites rather than soft ionic cations are responsible for stabilizing the enolate. This difference between enolate stabilization between Cu/ZnO alkali-promoted catalysts and zirconium dioxide isosynthesis catalysts is not surprising since alkali-promoted Cu/ZnO catalysts are a completely different catalytic system from zirconium dioxide. 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 hydroxide promoters over zirconium dioxide was found to decrease the formation of products from the condensation reaction (*9*). What zirconium dioxide and alkali-stabilized Cu/ZnO catalysts share in common is that the stabilization of an enolate is important to the chain growth process and that stabilization is achieved by a surface cation.

Maruya *et al.* (*4*) may have found 2-methylpropene production increased by the addition of NaOH to the zirconium dioxide surface, but since 2-methylpropene may be formed by two different paths, it is not clear why or how this increase took place. Indicators of the rate of condensation versus CO insertion such as the isosynthesis profile (*2*) and the intercept of the graphs in Fig. 2 for the labeled acetone (listed in Table 1) that have been used in this laboratory appear to be accurate in identifying the relative importance of this ratio.

The data in Table 4 also show that the more acidic the catalyst the more the branched C_3 intermediates (branched enolate and ketone) appear to be stabilized since the branched-to-linear ratio of the C_3 intermediates increases with increasing acidity. Mazanec proposed (*3*) that the relative stability of enolates on the surface could be predicted by the dehydration of 2-alcohols over the same catalyst. It was proposed (*3*) that enolate (I) (Fig. 1) leading to branched products through CO insertion was similar to an intermediate in the dehydration of 2-alcohol to 1-olefin, a base-catalyzed reaction. Therefore, basic catalysts were proposed to stabilized enolate (I) better than a more highly substituted enolate, such as (II), with a methyl group on the terminal carbon. However, the catalysts in this study have shown just the opposite results: the branched-to-linear ratio of C_3 intermediates is larger for the more acidic catalysts. In addition, the results of 2-alcohol dehydration (*2*) over the catalysts listed in Table 4 do not show a correlation between the fraction of 1-olefin from 2-alcohol dehydration and the fraction of branched enolate in the isosynthesis reaction.

The acid-modified zirconium dioxide is not listed in Table 4 because the addition of methanol so significantly altered the reaction selectivity that the methanol branched-to-linear results were probably not representative of the unaltered reaction. The relative rates of the four synthesis routes could not be solved for the acid-modified zirconium dioxide without getting a negative value for CO insertion into the linear-adsorbed aldehydes. Methanol addition effects three variables over acid-modified zirconium dioxide: the isosynthesis profile, which is the relative measure of the condensation reaction; the branched-to-linear ratio; and the concentration of C_4 and C_5 products. Methanol is known to adsorb on zirconium dioxide as methoxide, which as a basic species is likely to adsorb on a Lewis acid site. The poisoning of these sites with methoxide appears to reduce the frequency of the condensation reaction which is seen in the decrease of the isosynthesis profile. Since condensation appears to be an important contributor to chain growth on acid-modified zirconium dioxide, it is not unexpected that the overall production of C_4 and C_5 decreased with blocked acid sites. The simultaneous increase of the branched-to-linear ratio with these other changes indicates that before methanol was added condensation took place primarily on branched enolates leading to linear hydrocarbons. When condensation decreased, the importance of the CO insertion reaction increased relative to condensation, and the branched enolates transformed to ketones and formed branched C_4 products through CO insertion. Therefore, the unaltered acid-modified zirconium dioxide catalyst has a strong preference for condensation (as the value—50.2—of condensation versus CO insertion into labeled acetone would indicate) and a high ratio of branched C_3 intermediates to linear C_3 intermediates on the surface. Acid-modified zirconium dioxide continues the trend: the more acidic the catalyst, the more likely it is to undergo condensation versus CO insertion and the more branched enolates to linear enolates there are on the surface.

The other catalyst affected by methanol addition was also an acidic catalyst, 9% Sc_2O_3. Methanol adsorption on this catalyst did not appear to poison sites; in fact it seemed to make the catalysts more active: C_4 and C_5 hydrocarbon products increased. The branched-to-linear ratio decreased indicating that the additional methoxide available reacted with the enolates on the surface forming C_4 and C_5 products. Since there are more branched enolates on the surface of 9% Sc_2O_3 than linear enolates, this increase in condensation activity would lead to linear hydrocarbon formation.

V. CONCLUSIONS

Lewis acid sites enhance the condensation reaction by stabilizing the electron-rich η^3-enolate that reacts with the methoxide to form C_4 products. The more acidic the surface, the more branched C_3 intermediates there are versus linear C_3 intermediates. Therefore, the more acidic the catalyst, the greater the percentage of C_4 products made but not necessarily with the highest branched-to-linear ratio. Zirconium dioxide is an acid-base bifunctional catalyst and it is a balance of both of those properties which appears necessary for significant branched C_4 production.

VI. ACKNOWLEDGMENTS

This work was supported by the Division of Chemical Science, Office of Basic Energy Science, US Department of Energy, under Grant DE-FG05-86ER13604. The gas chromatograph and mass spectrometer detector were funded by a grant from Shell Companies Foundation.

REFERENCES

1. Tseng, S. C., Jackson, N. B., and Ekerdt, J. G., *J. Catal.* **109,** 284 (1988).
2. Jackson, N. B., and Ekerdt, J. G., *J. Catal.* **126,** 31 (1990).
3. Mazanec, T. J., *J. Catal.* **98,** 115 (1986).
4. Maruya, K., Maehashi, T., Haraoka, T., Narui S.,

Asakawa, Y., Domen, K., and Onishi, T., *Bull. Chem. Soc. Japan.* **61,** 667 (1988).

5. 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.), pp. 295–312, ACS Symposium Series 279, American Chemical Society, Washington, DC, 1985.
6. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C-W., and Herman, R. G., *J. Catal.* **116,** 195 (1989).
7. Tanabe, K., "Solid Acids and Bases," Academic Press, New York, 1970.
8. He, M-Y., and Ekerdt, J. G., *J. Catal.* **87,** 381 (1984).
9. Jackson, N. B., Ph.D. thesis, Department of Chemical Engineering, University of Texas, Austin, 1990.