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A Fischer-Tropsch Study of Supported Ruthenium Catalysts

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The effect of catalyst support on the activity and product selectivity of CO hydrogenation by ruthenium is discussed. The specific activity of supported ruthenium is dependent upon the nature of the support and on the metal loading. The specific activity for both CO conversion and CH_4 production increases with increasing metal particle size, obtained either by increasing the metal loading on a given support or by choosing a support which poorly disperses the metal. Supported catalysts with large particles are similar to unsupported ruthenium in activity, but not in selectivity. Product selectivity is characterized by olefin/saturate ratio, length of the hydrocarbon chain, and tendency to produce branched-chain hydrocarbons. Selectivity is a function of both the support and the metal loading. The degree of saturation in the products increases with increasing CO conversion. The length of the hydrocarbon chain is dependent upon temperature, pressure, and nature of the support, but not on the degree of CO conversion. Branched-chain hydrocarbons are produced utilizing acidic supports such as silica–alumina or zeolites, by subsequent isomerization of the initially formed straight-chain products. It is suggested that the support may alter the catalytic behavior of ruthenium through both electronic and dispersional effects.

INTRODUCTION

The rising importance of coal as an energy source has brought about renewed interest in processes for its conversion to clean fuels. One such scheme involves the reaction of coal with steam to produce synthesis gas, followed by the catalytic conversion of the carbon monoxide and hydrogen to hydrocarbons and chemicals. A significant volume of work has appeared on the catalytic reactions involved; the activities and types of products expected from the various metal or metal oxide catalysts seem to be fairly well established (*1*). One notable aspect of many Fischer–Tropsch catalysts thus far utilized, however, has been the low dispersion of the active metal component. Typical catalysts have consisted of metals on low-area supports (e.g., Ni, Co on kieselguhr) or on no support at all (Fe, Ru) (*2*). Relatively little information is available on the Fischer–Tropsch chemistry of Group VIII metals on high-area oxide supports.

There are several reasons why high-area supported catalysts are of interest and of potential practical importance: (i) The support may interact with the metal, changing its electronic properties and, concomitantly, its activity or selectivity. (ii) Metal loading or dispersion becomes a parameter which can be adjusted in order to study structure sensitivity of the reaction. (iii) Metal sintering can be reduced. (iv) Some of the catalytic metal species are sufficiently expensive that high dispersions and low loadings are an economic necessity.

Vannice has recently studied methana-

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tion and higher hydrocarbon synthesis over a series of Group VIII metals supported on alumina (*3*). In addition to demonstrating variations in selectivity among the metals, he compared their specific activities by normalizing the CO conversion or CH_4 production to the amount of metal available on the surface. Subsequent work has suggested that the specific activity of the catalytic metal is not a fixed quantity, however, and evidence suggests that both the nature of the support and the particle size are important in methanation activity (*4*, *5*).

The influence of support and particle size apparently depends upon the metal. For example, the specific activity for methanation with platinum catalysts increases drastically with increasing dispersion, with only a small effect from support variation. By way of contrast, methanation activity with palladium was found to be much less sensitive to dispersional effects and more sensitive to the support, with acidic supports producing the most active catalysts (*4*). Nickel catalysts are again different; neither the nature of the support nor the effect of dispersion was observed to be as important as with Pt or Pd. However, supported Ni gave more long-chain hydrocarbons than bulk Ni. Interestingly, specific methanation activity with nickel increased with increasing particle size (opposite that observed with Pt), and the existence of an optimum particle size has been suggested (*5*).

In contrast to methanation, much less seems to be known about effects of the support on the nature or distribution of longer chain hydrocarbons. Most research in this area (as in the above-mentioned work with Ni) has concentrated on a breakdown of yield vs hydrocarbon number, with little concern for finer details of the product distribution. The present work looks at a number of supported ruthenium catalysts and concentrates on the following points: (i) the dependence of the specific activity for CO conversion on support and metal loading; (ii) the effect of support, temperature, and metal loading on the olefin/paraffin ratio and on the length of the hydrocarbon chain. (iii) the variation in yield of branched-chain hydrocarbons.

The nature and extent of these effects are of interest, both from practical and theoretical standpoints. Not only is there the possibility of altering product distributions by judicious choice of support and reaction conditions, but also some information is provided regarding initial product formation and reaction mechanism.

There are several reasons why ruthenium was chosen for this study. It has high specific activity (the highest of the Group VIII metals for methanation) (*3*) and is noted for its ability to produce long-chain hydrocarbons (*1*, *2*). This latter effect can be demonstrated even with reactors operating at low pressure. The products have little or no oxygen content, thus simplifying analysis. Supported ruthenium is reduced relatively easily, even at low loadings. Finally, ruthenium has been reported to have an intriguing "dual nature activity" which relates to an enhanced activity for methanation following brief exposure to oxygen (*6*, *7*). This dual nature was also observed in the present study.

EXPERIMENTAL

Catalysts were tested in a fixed-bed, downflow microreactor constructed of stainless steel. The heated reactor section was a pipe 12 in. long and 0.25 in. inside diameter. The catalyst charge was typically 0.75 g and filled approximately the center 2 in. of the reactor. Calcined quartz wool was used to retain the catalyst in place. The reactor pressure was held at 4 atm, with the reaction temperature adjusted from 175 to 300°C. The reaction mixture, $H_2(67\%)/CO(33\%)$ (Linde Custom Grade Mixture) was used without further purification. The possibility that contamination could have occurred from metal carbonyls in the feed was subsequently checked by mass spectrometric, infrared, and colorimetric methods. No evidence was found for these species at levels sufficient to alter the composition of the catalyst, and no evidence for metal deposits (mirroring) was found on either the catalyst or the quartz wool plug. As a final check, high-area sieve traps were placed upstream of the reactor and several catalysts were rerun with no change in results. Flow rate was set at 30 ml min^{-1} ($\sim$1200 GHSV). Products were analyzed (C_1–C_4, plus iso- and *n*-pentane) utilizing a small gas chromatograph (Carle, Model 8515).

All but two of the catalysts were prepared by impregnation, using $RuCl_3$ hydrate dissolved in water at the concentration appropriate to yield 1 ml of solution/g of catalyst. The solution was not acidified. The remaining two catalysts were prepared by ion exchange of Ru (NO) $(NO_3)_3$ with NaX and NaY molecular sieves, using a 0.01 *M* aqueous solution. Exchange was effected at 75°C, with successive changes of stock solution until decoloration of the solution ceased. Metal loading was estimated by atomic adsorption at $\sim$2.5% for NaX and $\sim$6% for NaY, by weight. The wet catalysts (from impregnation or exchange) were dried under vacuum at 110°C for a minimum of 4 hr prior to insertion in the reactor.

Pretreatment of the catalyst consisted of heating in flowing H_2 at 100°C for 1 hr, 250°C for 1 hr, and 450°C for 1 hr. One exception to this was silica-supported ruthenium, which was reduced at a maximum of 350°C to avoid sintering (*8*). The catalyst was then cooled to the appropriate temperature with H_2 flowing, followed by switching to H_2/CO flow. Twenty to thirty minutes passed prior to sampling the product stream, and subsequent samples were taken at longer times to observe catalyst deterioration or any changes in product distribution. Prior to measurements at a different reaction temperature, the catalyst was rereduced at 450°C for 1 hr.

Most of the supports used were obtained commercially. Thoria was prepared by dissolving the nitrate in H_2O, precipitating the hydroxide with NH_4OH, and subsequently calcining to ThO_2 (surface area, 32 m^2/g). Thoria–alumina (10% ThO_2) and chromia–alumina (15% Cr_2O_3) were prepared by impregnation of Al_2O_3 with $Th(NO_3)_4$ and $(NH_4)_2Cr_2O_7$, respectively, followed by calcination. Catalyst supports were either ground, or pressed and ground, to 20–60 mesh prior to impregnation.

An unsupported ruthenium catalyst was prepared from RuO_2 hydrate (Matthey-Bishop, Inc.) and was treated in the same manner as the supported catalysts. The hydrated form was reported to have a high surface area ($\sim$85 m^2/g); however, this area was rapidly lost during catalyst pretreatment (dehydration and reduction), resulting in a very poorly dispersed catalyst (see Table 1).

Metal surface area measurements were obtained by H_2 chemisorption using the isotherm method at 100°C (Digisorb, Model 2500). Measurements were made on fresh catalysts of the same batch used for the microreactor studies. No surface area measurements were obtained with spent catalysts. The standard pretreatment for the surface area measurements was evacuation at 250°C for 4 hr followed by heating in H_2 at 400°C for 4 hr. The catalyst was then evacuated at 400°C and cooled to 100°C, followed by H_2 chemisorption measurements. Surface areas were also measured by CO chemisorption; however, these were consistently higher (factor of 2 or 3) utilizing this method than those obtained with H_2. This may be attributable to multiple CO adsorption or to other unexplained effects (*9*, *10*). Only H_2 chemisorption data were used in calculating catalyst activities.

RESULTS

Catalyst Activity

The CO conversion levels achieved in the present work (typically 10–25% at 250°C)

TABLE 1

Activity of Supported Ruthenium Catalysts (250°C)

Catalyst	CO conversion (%)	Dispersion (%)	N_{CO} (sec^{-1}) $\times 10^3$	N_{CH_4} (sec^{-1}) $\times 10^3$
0.5%/Al_2O_3[a]	2.8	60	28.1	10.4
1.25%/Al_2O_3[a]	11	44	60.3	19.5
1.8%/Al_2O_3[a]	18	44	68.5	20.1
2.5%/Al_2O_3[b]	26	34	89.1	37.1
2.5%/Al_2O_3[c]	22	23	117	43.3
1.5%/SiO_2	6.3	13.8	92	32.2
2.5%/SiO_2	12.9	8.5	183	73.2
2%/SiO_2–Al_2O_3[d]	11.5	11	154	67.0
2%/SiO_2–Al_2O_3[e]	12	9.5	148	49.3
2%/Cr_2O_3–Al_2O_3[f]	20	24.5	114	33.5
2%/Cr_2O_3–Al_2O_3[g]	9.8	49	30.8	7.7
2.8%/ThO_2	19	29	68.5	19.6
2%/ThO_2–Al_2O_3[h]	16	27	89	31.8
2.5%/NaX sieve	18	22	97	33.4
2.5%/Ultrastable sieve	21	35	75.4	26.9
Unsupported Ru	14.5	0.3	193	143

[a] γ-Alumina, pore diameter (p.d.) = 118 Å.

[b] γ-Alumina, p.d. = 137 Å.

[c] γ-Alumina, p.d. = 44 Å.

[d] 10% SiO_2.

[e] 85% SiO_2.

[f] 15% Cr_2O_3, commercial preparation.

[g] 15% Cr_2O_3, laboratory preparation.

[h] 10% ThO_2.

are higher than are generally maintained when operating under differential reaction conditions. This was done to allow comparison of catalysts having a broad range of activities, while maintaining nearly constant bed volumes and flow conditions, and product levels adequate for the sensitivity range of the gas chromatograph. It should be emphasized that the results were intended to demonstrate qualitative trends rather than quantitative kinetic data. However, even qualitative trends can be rendered invalid in the presence of severe temperature or diffusion effects. For this reason, several tests were run on catalysts having CO conversions of 20–25% including altering the particle size, altering the flow rate at constant space velocity, and diluting the catalyst with unimpregnated support (Koros–Nowak technique). In only one case was evidence obtained for catalyst overheating, this being with 6.25% Ru/Al_2O_3 at 250°C and higher temperatures. The product distribution shifted strongly toward methane, and thermocouples mounted on the catalyst tube showed evidence of overheating. The catalyst was subsequently sintered in air to reduce its activity prior to use.

Table 1 compares CO conversion, metal dispersion, and CO and CH_4 turnover frequencies for a series of supported ruthenium catalysts operating at 250°C. Data were obtained 20–30 min after initiating H_2/CO flow over the catalyst; this minimized catalyst deactivation effects, which were often observed with catalysts after several hours on stream. CO conversion levels are consistently underestimated, since isopentane and *n*-pentane are the only C_5+ products analyzed. The error caused by omission of the remaining C_5+ products is small, how-

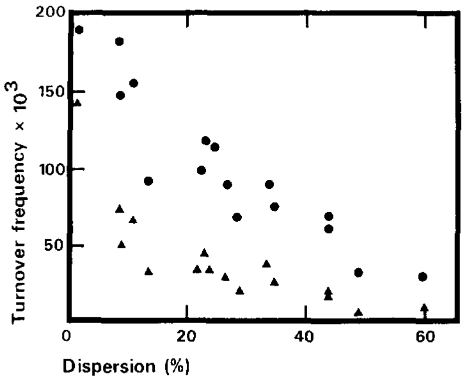

FIG. 1. Catalyst turnover frequencies (per second) as a function of ruthenium dispersion at 250°C. (●) CO conversion, (▲) CH_4 production.

ever, since heavy products are significant mostly at low temperatures where conversions are also generally low. Since this is a systematic error, it should not greatly affect relative comparisons between catalysts.

From Table 1 one sees roughly a sevenfold variation in specific activity for CO conversion between the most and least active catalysts used in this study. Excluding unsupported ruthenium, roughly the same variation is observed with methanation activity. A perusal of the data suggests that poorly dispersed catalysts actually have higher specific activities. This is shown more clearly in Fig. 1. Despite some scatter in the data, there is a clear correlation of increasing activity with decreasing dispersion (increasing metal particle size). Scatter in the data could be due to metal–support interactions, to uncertainties in the surface area measurements, or (more likely) to both. The dependence of CO conversion on dispersion for supported catalysts extrapolates well to the turnover obtained with the poorly dispersed unsupported Ru catalyst. This is less true for the methanation activity, where unsupported Ru appears to have an anomalously high methanation rate.

It is useful to compare specific activities obtained in the present work with Vannice's Ru/Al_2O_3 results (*3*). This is best achieved with methanation activity, for which the kinetic parameters were determined. Vannice's value of 0.181 sec^{-1} at 275°C was based on the surface area of a spent catalyst having 6% dispersion. The activity based on the surface area of a fresh catalyst is more comparable to the present work and would be lower, 0.149 sec^{-1}, with a dispersion of 7.3%. After correcting for the differences in reaction temperature (250 as opposed to 275°C), feed ratio ($H_2/CO = 2/1$ as opposed to 3/1), and reactor pressure (4 as opposed to 1 atm), a value of 0.131 sec^{-1} is predicted from the Vannice work. This is to be compared with a value of approximately 0.07 sec^{-1} predicted from Fig. 1 for a catalyst having 7.3% dispersion. Considering the approximations made and the decrease in methanation tendency (increase in heavy products) with increasing pressure, variation within a factor of 2 should probably be considered good agreement.

Catalyst Selectivity

Table 2 presents product distributions from a Ru/SiO_2 catalyst. These are typical

TABLE 2

Product Distributions from 2.5% Ru/SiO_2 Catalyst

	Product (mol%)		
	225°C	250°C	275°C
C_1 (Methane)	63	71	80.5
C_2 (Ethane)	4.8	7.6	6.6
C_2 (Ethylene)	1.3	0.3	0.1
C_3 (Propane)	3.4	6.6	5.1
C_3 (Propylene)	8.9	3.4	1.7
C_4 (*n*-Butane)	4.1	4.1	2.5
C_4 (Isobutane)	0.0	0.0	0.0
C_4 (Butene-1)	7.8	1.6	0.3
C_4 (*cis*-Butene-2)	0.9	1.0	0.8
C_4 (*trans*-Butene-2)	1.7	1.0	0.7
C_4 (Isobutylene)	0.0	0.0	0.3
C_4 (1,3-Butadiene)	0.0	0.0	0.0
C_5 (*n*-Pentane)	4.1	3.4	1.4
C_5 (Isopentane)	0.0	0.0	0.0
CO conversion (%)	3.1	12.9	17.6

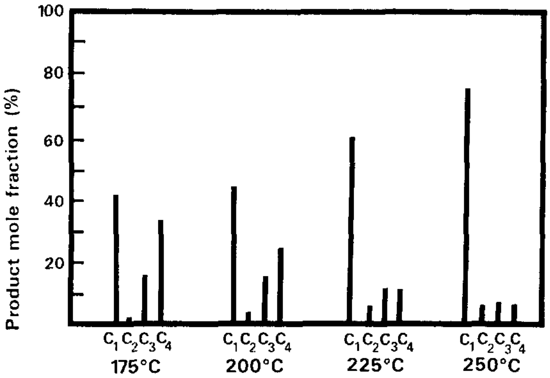

FIG. 2. Product distributions by carbon number. Catalyst is 6.25% Ru/Al_2O_3.

of those obtained in the present work. The temperatures shown were found to be optimum for observing a wide range of products in sufficient yield for quantitative determination. Attention is called to the following aspects of the distribution: (i) CO conversion increases with increasing temperature; (ii) CH_4 is the predominant product at all temperatures; (iii) the mole fraction of CH_4 in the total product increases with increasing temperature; (iv) low temperatures enhance the yield of olefins relative to saturates; (v) the ethylene/ethane ratio is significantly lower than the propylene/propane or butene/butane ratio; (vi) the yield of 2-butenes increases relative to 1-butene with increasing temperature; (vii) no branched products are observed.

Figure 2 emphasizes the effect of temperature on the length of the hydrocarbon chain. The catalyst used, 6.25% Ru/Al_2O_3, had a higher metal loading than normally used and was selected simply to demonstrate hydrocarbon chain length over a wide temperature range. The initial activity of this catalyst showed evidence of catalyst overheating; the activity was then decreased by sintering the catalyst in a N_2/O_2 atmosphere prior to obtaining the data used in the figure. No surface area data were obtained on this sintered catalyst, however, and thus it is not included in the tables.

The variation in product composition (chain length) is a consequence of the different activation energies for methanation and overall CO conversion (*3*, *11*). The main point to be stressed here is that results from various ruthenium catalysts must be compared at the same reaction temperature in order to assess effects such as support interactions on the product distributions.

Since increasing the temperature also increases the CO conversion level, it is reasonable to ask whether the trends observed are strictly due to temperature or are a combination of temperature and CO conversion effects. This is important in the present work, since catalysts have different loadings, dispersions, and activities; under the same reaction conditions, CO conversions quite naturally vary. To address this, some aspects of the product distributions will be evaluated as a function of CO conversion level at a fixed temperature. Certain characteristics of the distribution will be shown to be a function of conversion, while others are not. Provided that CO conversion is not so high that catalyst overheating occurs, the effect of conversion level on catalyst product distribution is quite predictable. It can thus be separated out, allowing comparison of other effects, such as catalyst–support interactions, to be made.

For comparison of product selectivity between catalysts, a reaction temperature of 250°C has been used, although data at other temperatures will also be presented when appropriate. Since ruthenium catalysts do not produce oxygen-containing compounds, product distributions will be characterized and compared by the following: (a) degree of hydrogenation: relative yield of olefins vs saturates; (b) chain length: C_2+/C_1 ratio; (c) degree of isomerization: ratio of isoalkanes/*n*-alkanes.

Olefin Yields

Table 3 shows olefin/saturate ratios for C_2–C_4 hydrocarbons produced from ruthenium on a variety of supports at 250°C. A large variation in olefin/saturate compositions is apparent with these catalysts; for example, propylene varies from 75% of the total C_3 product for Ru/Cr_2O_3–Al_2O_3 to approximately 17% for Ru/SiO_2–Al_2O_3 (10% SiO_2). The propylene/propane ($C_3^=/C_3$) ratio has been found to be the most convenient criterion for olefin production, although the same trends are observed in the C_2 and C_4 ratios. Compared with the C_3 distribution, ethylene/ethane ratios are consistently much lower and less sensitive to catalyst changes, while C_4 ratios are complicated by the existence of more than one butene product.

TABLE 3

Olefin/Saturate Ratios as a Function of Catalyst Support

Catalyst	Ethylene/ ethane	Propylene/ propane	Butene-1 *n*-butane
0.5%/Al_2O_3[a]	0.24	1.95	1.0
1.25%/Al_2O_3[a]	0.08	1.12	0.60
1.8%/Al_2O_3[a]	0.06	0.75	0.43
2.5%/Al_2O_3[b]	0.02	0.33	0.21
2.5%/Al_2O_3[c]	0.05	0.70	0.46
1.5%/SiO_2	0.15	1.70	1.31
2.5%/SiO_2	0.04	0.52	0.39
2%/SiO_2–Al_2O_3[d]	0.02	0.19	0.21
2%/SiO_2–Al_2O_3[e]	0.08	0.84	0.48
2%/Cr_2O_3–Al_2O_3[f]	0.05	0.65	0.33
2%/Cr_2O_3–Al_2O_3[g]	0.27	3.0	1.5
2.8%/ThO_2	0.13	1.2	0.62
2%/ThO_2–Al_2O_3[h]	0.04	0.67	0.36
2.5%/NaX sieve	0.04	0.69	0.44
2.5%/Ultrastable sieve	0.02	0.20	<0.02
Unsupported Ru	0.30	3.8	2.4

[a] γ-Alumina, p.d. = 118 A.
[b] γ-Alumina, p.d. = 137 A.
[c] γ-Alumina, p.d. = 44 A.
[d] 10% SiO_2.
[e] 85% SiO_2.
[f] 15% Cr_2O_3, commercial preparation.
[g] 15% Cr_2O_3, laboratory preparation.
[h] 10% ThO_2.

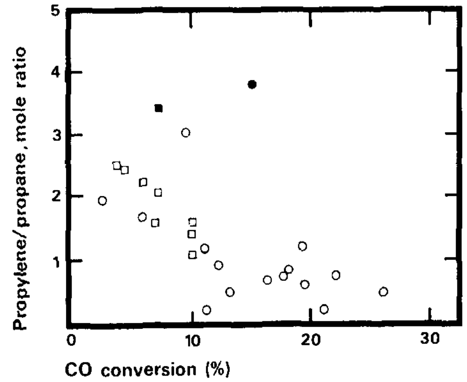

FIG. 3. Olefin/saturate ratio from C_3 product distribution for supported and unsupported ruthenium catalysts. (○) Supported Ru, 250°C; (□) supported Ru, 225°C; (●) unsupported Ru, 250°C; (■) unsupported Ru, 225°C.

In addition to the variation in olefin production with support, Table 3 shows that, on a given support, an increase in metal loading is accompanied by an increase in the saturated fraction of the product. The only observed exception is the unsupported ruthenium catalyst which produces an anomalously high fraction of olefins. Additional experiments in which the reactant flow was varied showed that while the conversion of CO was inversely proportional to space velocity, the unsaturate/saturate ratio was dependent on space velocity, with higher flows producing more olefins.

The variations in olefin yield with temperature, metal concentration, and space velocity suggest that a relationship exists between unsaturate production and CO conversion level. Figure 3 shows the $C_3^=/C_3$ ratios plotted as a function of CO conversion for the catalysts listed in Table 1. There is an apparent reverse correlation between CO conversion level and olefin yield. Data obtained from a few of these catalysts at 225°C is included to demonstrate that these results mesh reasonably well with the data at 250°C, when conversions are comparable. Results from other catalysts less well characterized showed results consistent with this dependence of olefin yield on conversion. Thus, the figure suggests that variations in olefin fractions observed with a variety of supports are due primarily to variations in CO conversion (different dispersions, loadings, and/or activities) rather than to specific metal–support interactions. Catalysts with $C_3^{=}/C_3$ values far from the general trend may represent cases where metal–support interactions are important. Most notable of these supports are Cr_2O_3–Al_2O_3 and ThO_2, producing a high olefin fraction, and silica–alumina (10% silica), producing a low olefin fraction. Again, one notes in Fig. 3 the anomalously high yield of olefins with unsupported ruthenium relative to the supported ruthenium catalysts.

Methanation vs Fischer–Tropsch

Two variables which have strong influence on hydrocarbon chain length with ruthenium are pressure and temperature. Ruthenium, operating at several hundred atmospheres of pressure, has been shown to produce paraffins of high molecular weight (*1*). This is in part a thermodynamic effect (*12*) and is aided by lack of carbonyl formation with ruthenium (*1*). The effect of temperature on chain length was demonstrated previously in Fig. 2 for a Ru/Al_2O_3 catalyst. There is a pronounced shift to lighter products, particularly methane, with increasing temperature.

TABLE 4

Fischer–Tropsch/Methanation Ratios of Supported Ruthenium Catalysts (250°C)

Catalyst	Weight ratio, C_2+/C_1
$0.5\%/Al_2O_3$[a]	1.7
$1.25\%/Al_2O_3$[a]	2.1
$1.8\%/Al_2O_3$[a]	2.3
$2.5\%/Al_2O_3$[b]	1.4
$2.5\%/Al_2O_3$[c]	1.7
$1.5\%/SiO_2$	1.9
$2.5\%/SiO_2$	1.5
$2\%/SiO_2$–Al_2O_3[d]	1.3
$2\%/SiO_2$–Al_2O_3[e]	2.0
$2\%/Cr_2O_3$–Al_2O_3[f]	2.4
$2\%/Cr_2O_3$–Al_2O_3[g]	3.0
$2.8\%/ThO_2$	2.5
$2\%/ThO_2$–Al_2O_3[h]	1.8
2.5%/NaX sieve	1.9
2.5%/Ultrastable sieve	1.8
Unsupported Ru	0.35

[a] γ-alumina, p.d. = 118 Å.
[b] γ-alumina, p.d. = 137 Å.
[c] γ-alumina, p.d. = 44 Å.
[d] 10% SiO_2.
[e] 85% SiO_2.
[f] 15% Cr_2O_3, commercial preparation.
[g] 15% Cr_2O_3, laboratory preparation.
[h] 10% ThO_2.

Table 4 presents data on the product weight ratio, C_2+/C_1, for the catalysts characterized in Table 1. With a few exceptions, this ratio falls between 1.25 and 2.5, with many different catalysts near 1.8. The variation in chain length does not appear to depend strongly or in any consistent manner on the nature of the support. In order to determine the possible effect of degree of CO conversion on chain length, Fig. 4 shows the measured C_2+/C_1 ratios as a function of conversion level at 250°C. The plot displays considerable scatter, but

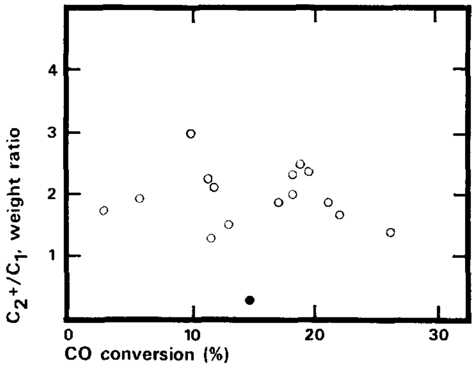

FIG. 4. Yield of Fischer–Tropsch products relative to methane for supported and unsupported ruthenium catalysts at 250°C. (○) Supported Ru; (●) unsupported Ru.

there is no apparent correlation between chain length of the product and amount of CO converted. It is interesting to note that the catalysts producing high yields of long-chain products, Ru/Cr_2O_3–Al_2O_3 and Ru/ThO_2, are the ones shown previously to produce higher than normal olefin yields. However, Fig. 4, together with the conclusions drawn from Fig. 3, imply that olefin yield and chain length do not in general correlate. This is particularly apparent with unsupported ruthenium, which has both a high methanation tendency and a large fraction of unsaturates in the C_2+ products. One can also see from comparison of Tables 1 and 4 that no consistent relationship between chain length and metal particle size (dispersion) emerges.

Isomerization Activity

With most of the supported ruthenium catalysts tested, branched-chain hydrocarbon production was far below that predicted by thermodynamics. Indeed, with many catalysts, isobutane and isopentane were below detection limits. Exceptions to this were found only for ruthenium on silica–alumina or zeolite supports. Table 5 presents isobutane/*n*-butane and isopentane/*n*-pentane ratios for those catalysts found to produce branched-chain products. These supports have the common characteristic of being highly acidic. One notes the importance of the silica/alumina ratio of the support for both zeolites and silica–alumina. The silica–aluminas appear less active than the zeolites in producing methyl-branched products, consistent with the relative surface acidities. There also is a significant difference in branched chain yield with the NaY sieve support, depending upon whether Ru is added by impregnation or ion exchange.

TABLE 5

Production of Branched-Chain Hydrocarbons (250°C)

Catalyst	iC_4/nC_4	iC_5/nC_5
2.5%/NaX sieve	0.01	0.01
Ion-exchanged/NaX sieve	0.01	0.01
2.5%/NaY sieve	1.20	3.0
Ion-exchanged/NaY sieve	0.30	0.80
2.5%/Ultrastable sieve	3.5	13.8
1.8%/Al_2O_3 + Ultrastable sieve	4.0	11.9
2%/SiO_2–Al_2O_3[a]	0.01	0.01
1.25%/SiO_2–Al_2O_3[b]	0.06	0.34
2%/SiO_2–Al_2O_3[c]	0.16	0.57
Thermodynamic equilibrium	0.75	3.3

[a] 10% SiO_2.

[b] 74% SiO_2.

[c] 85% SiO_2.

Perhaps the most interesting result is that obtained from a catalyst consisting of 1.8% Ru/Al_2O_3 mechanically mixed with an ultrastable sieve support. Products from this catalyst were as rich in isobutane and isopentane as those obtained from ruthenium impregnated directly onto the ultrastable sieve. This strongly suggests that isomerization occurs subsequent to and downstream from initial straight-chain product formation on the ruthenium metal site.

DISCUSSION

The results of this study suggest three ways in which supports can affect activity or selectivity of ruthenium catalysts for Fischer–Tropsch synthesis. (i) Support interactions may alter the electronic structure of the metal. (ii) The metal disperses differently on various supports, important since the reaction appears to be mildly structure sensitive. (iii) The support may adsorb and alter reaction products downstream of the metal site.

Evidence for electronic structure changes due to the support is not plentiful and, like the present work, is generally indirect (*13*). The main evidence here is provided by the difference (in activity and selectivity) between supported and unsupported ruthenium. Supported catalysts which deviate strongly from observed trends (e.g., Ru/Cr_2O_3–Al_2O_3) also provide evidence that the support in some instances can affect the catalytic properties of the metal.

While not specifically a support effect, the "dual nature activity" of ruthenium also provides evidence for changes in activity with changes in electronic structure. The exposure of ruthenium to oxygen for brief periods has been found to enhance its activity as a methanation catalyst (*6*, *7*). This effect was also observed in the present study, although not in a quantitative fashion. Brief exposures of the ruthenium catalysts (supported and unsupported) to oxygen resulted in enhanced CO turnover; the yields of methane relative to heavy products, however, were not strongly affected. It appears that this increase in catalyst activity following oxygen treatment is an increase in specific activity as well. Taylor *et al.* (*6*) showed that changes in ruthenium dispersion were not the cause of the dual nature activity, and surface reconstruction or support interactions were implicated. It should be pointed out, however, that the reduced state they described is different from the present work, since they observed poor activity for the CO/H_2 reaction with their "reduced" ruthenium.

Brown and Gonzales, in an infrared study, observed CO adsorbed on silica-supported ruthenium (*8*). In the presence of oxygen, new CO absorption peaks appeared at higher frequencies. They suggested that ruthenium, existing either as an oxide or perturbed by a nearby oxygen, adsorbs CO less strongly (CO stretch appears at higher frequencies) than does reduced, unperturbed ruthenium. Vannice has suggested that weakly held CO (linear form) is more reactive than the more strongly held CO (bridged form) (*4*, *5*). While this effect is different from that of oxygen perturbation of ruthenium, the increase in activity with decrease in metal–carbon bond strength follows a consistent trend. One possible explanation advanced (*14*) is that hydrogen and carbon monoxide compete for available sites; decreasing the metal–carbon bond strength could make hydrogen chemisorption more competitive. This should increase the reaction rate, since H_2 (or H) is involved in the rate-determining step.

The effect of oxygen in altering the electronic structure of ruthenium raised the possibility to this author that oxide supports on which ruthenium is impregnated might conceivably alter the electronic character of the ruthenium in a similar manner. That this is not the case is evidenced by the lower specific activity of supported ruthenium relative to the unsupported case. Indeed, the decrease in specific activity with decreased metal loading suggests that the more intimate contact of the metal with the support may have an inhibiting effect on CO conversion. This could explain the poor activity observed by Taylor *et al.* for reduced ruthenium at very low loadings (*6*). The enhanced methanation activity of supported Ru following O_2 exposure provides further evidence, of course, that oxide supports do not provide stabilization of the higher activity state of ruthenium.

For the catalyst supports used in this study, no evidence was found for a large variation in specific activity at comparable ruthenium dispersions. This suggests either that electronic support interactions with ruthenium are only of modest importance for moderate size metal particles, or that the effect of the support on the ruthenium particle is relatively constant. This contrasts with the effect of support on palladium methanation catalysts and is more in line with the support effects with platinum and nickel reported by Vannice (*4*, *5*). No activity increases were observed in the present study with highly acidic supports; this also contrasts with the results from Pd (and to a lesser extent, Pt).

An aspect of ruthenium–support interactions which appears to be important is the extent to which the support disperses the metal upon impregnation. The decrease in specific activity with increasing dispersion as demonstrated in Fig. 1 suggests a dependence of the activity on metal particle size. Since electronic properties of the ruthenium cluster can be expected to vary as its size varies, separation of electronic from dispersional effects cannot be made. However, the data suggest that electronic factors, if they exist, are mostly inherent in the metal cluster itself and are not strongly dependent on electron transfer with the support.

The conclusion that large ruthenium aggregates have higher specific activities for CO conversion than do smaller particles is in agreement with the data of Dalla Betta *et al.* (*11*). They found an increase in steady-state activity with increasing particle size for Ru/Al_2O_3 catalysts. Such a particle size dependence was not found for initial activity, however (*7*), suggesting that the present data were also obtained at or near steady-state conditions. The increase in activity with particle size for ruthenium is opposite to and of lesser magnitude than that observed with Pt and Pd methanation catalysts; it is in accordance with the increase in activity for Ni/SiO_2 catalysts with increasing crystallite size. Vannice has suggested with Ni that an optimum particle size may exist, since large unsupported Ni crystallites have low activity (*5*). Such an optimum particle size was not found in the present work with ruthenium.

In addition to activity differences, there are some selectivity differences traceable to the support. Support acidity, however, does not appear to be important other than to produce branched products. The most obvious differences with support are the variations in olefinic fraction of the product; these are due predominantly to the level of CO conversion and thus to the metal dispersion, rather than to specific support interactions. Two catalysts producing abnormally high fractions of olefins (Ru/Cr_2O_3–Al_2O_3 and Ru/ThO_2) also produced higher fractions of heavy products. This could be due to metal–support interaction, and further catalyst characterization is needed. It is interesting to note that the converse is not true, i.e., catalysts with lower olefinic yields do not necessarily show a shift in product distribution toward lighter hydrocarbons or methane (unless the temperature is increased).

The observation that olefin yields are a function of CO conversion while product chain length is independent of conversion level suggests that olefins are probably precursors of saturated hydrocarbon products, except for CH_4. These are probably almost exclusively terminal olefins, since other olefins (i.e., butene-2) are only observed at the more elevated temperatures where thermodynamic equilibration appears to be occurring. The increase in saturates with increasing conversion is probably due to hydrogenation of the olefin downstream of the original Ru site. The independence of chain length on conversion level suggests the relative difficulty of inserting an olefinic species into the chain compared with simply saturating it. Ethylene may be an exception to this, and its abnormally low yield may indicate ease of incorporation into the chain as well as a tendency to saturate. Once saturated, hydrocarbons are known to be not easily incorporated during chain growth (*15*).

The lack of correlation between chain length and metal particle size is also of some interest. Since some theories of chain growth assume combination of carbon atoms on adjacent metal sites (*15*), metal particle size effects could be important, and one might anticipate shorter chains with more highly dispersed catalysts. It is likely that the catalysts of highest dispersion in the present study still have particles too large for such an effect to be observed. It would be of interest, however, to study product distributions from a truly monodispersed catalyst.

The anomalous behavior of unsupported Ru is an area for future study. Unsupported

Ru is more selective toward methane production than supported Ru, yet the remaining small fraction of heavy products is high in unsaturates. Since CH_4 is the most highly hydrogenated hydrocarbon, its presence in high yield might lead one to expect a preference for saturation of the remaining C_2+ products. The difference in product distribution from unsupported Ru may be due to different mechanisms for methanation and heavy product synthesis, or possibly to variations in surface sites which favor certain types of products. These differences between supported and unsupported ruthenium catalysts simply serve to remind us of our ignorance regarding the hydrogenation of the CO molecule.

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