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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: METHOD FOR PREPARING COBALT-CONTAINING HYDROCARBON SYNTHESIS CATALYST

(57) Abstract

The activity of supported cobalt catalysts for hydrocarbon synthesis is maximized by carrying out the reduction at conditions that keep both the partial pressure of water vapor and the maximum reduction temperature below critical maximum values. For titania supported cobalt catalysts, the preferred maximum water partial pressure is one atmosphere and the preferred maximum reduction temperature is 375 °C.

Method for preparing cobalt- containing hydrocarbon synthesis catalyst

FIELD OF THE INVENTION

This invention relates to activating cobalt containing hydrocarbon synthesis catalysts. More particularly, this invention relates to maximizing hydrocarbon synthesis catalyst activity by controlling the temperature in the activation step and by controlling the maximum water partial pressure produced during the activation step. Still more particularly, this invention relates to reducing a reducible cobalt compound, that produces water during reduction, to a catalytically active state under conditions that limit the water partial pressure produced during the reduction step.

BACKGROUND OF THE INVENTION

The activation of hydrocarbon synthesis catalysts is widely reported in the literature. Activation usually involves reduction, in a flowing hydrogen or hydrogen containing gas stream, at elevated temperatures. The reduction proceeds from a reducible metal compound, usually, but not necessarily the metal oxide. Thus, the literature reports reduction of metal oxides to the elemental or active form of the metal as well as reduction from metal compounds, impregnated either as water soluble or hydrocarbon soluble salts.

For example, hydrocarbon synthesis catalysts are usually prepared by depositing a metal, such as cobalt or other Group VIII metals onto a support, by techniques such as impregnation, the metal being in a water soluble (e.g., cobalt nitrate) or hydrocarbon

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soluble (e.g., cobalt carbonyl) form. The catalyst is usually dried to eliminate the solvent, but reduction (or activation) does not occur during the drying step even though a hydrogen containing gas may be used as the drying agent.

Once having the metal compound impregnated onto the support, activation by reducing to the elemental or catalytically active form of the metal may proceed directly from the metal compound, or the metal compound may be converted to a more easily reducible form, such as the oxide and then reduced to its elemental or catalytically active form. In either case the metal compound must be reducible to its catalytically active form; the oxide is one form of reducible metal compound.

SUMMARY OF THE INVENTION

In accordance with this invention, a highly active hydrocarbon synthesis catalyst is prepared by reducing a metal compound, at elevated temperatures and pressures and in the presence of a hydrogen containing gas stream, to its catalytically active form and maintaining the water partial pressure during the reduction at less than about five atmospheres. In a preferred embodiment, the reduction step, which is the catalyst activation step, is carried out below about 550°C, and preferably in the range of about 250°-425°C.

While water vapor can be introduced into the reduction step with the hydrogen containing gas, either on purpose as steam or as a contaminant, the bulk of the water vapor comes from the metal compound being

reduced, usually an oxygen containing compound, the most common compound being the metal oxide form.

In another embodiment of this invention the variables affecting water partial pressure during the reducing or activating step have been identified, and therefore, a determination of the water partial pressure can be made beforehand and a catalyst of high activity produced. These factors are: weight percent of the metal compound, hydrogen containing gas flow rate and water content thereof, rate of temperature rise during the reducing/activating step, total pressure and hydrogen partial pressure, and reactor type.

Thus, the activation procedure is not dependent on the particular support or particular structural promoter employed, and this invention is applicable to the use of any support or structural promoter generally used in the preparation of hydrocarbon synthesis catalysts. For example, inorganic oxides, particularly difficultly reducible, inorganic oxides selected from the metals of Groups III-VI of the Periodic Chart of the Elements are often used as supports for hydrocarbon synthesis catalysts, and they may be used in the method of this invention. Additionally, structural promoters employed in the preparation of catalysts by micelle technology wherein the structural promoter may be similar to materials used as supports but act instead as providing a structure for the catalytic metal (the catalytic metal and the material being composited as an aggregate rather than the material supporting the catalytic metal). A detailed description of micelles is provided in the Encyclopedia of Science and Technology, 6th Ed., McGraw-Hill publisher, New York 1987, and in Preparation of Catalysts IV by Ravet et al,

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505-507, Delmon, Grange, Jacobs, and Poncelet Eds.,
Elsevier, 1987.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of percent H_2O in the exit
gas v. time for two different hydrogen reduction flow
rates at 450°C, 100 psig for Catalyst A.

Figure 2a is a plot of relative catalyst
activity at 200°C v. maximum water partial pressure in
atmospheres, for reduction in hydrogen with temperature
ramped from ambient to a maximum of 450°C for Catalyst
A.

Figure 2b is also a plot of relative catalyst
activity at 190°C v. maximum water partial pressure but
concentrates on partial pressures up to 3 atmospheres,
for Catalyst B, reduced in hydrogen with temperatures
ramped from ambient to a maximum of 370-400°C.

Figure 3 is a plot of relative catalyst
activity v. maximum reduction temperature for Catalysts
A and B. XPS signal ratio for Catalyst B v. maximum
reduction temperature is also shown. Water partial
pressure was less than 0.24 atm during these tests.

Figure 4 shows a derivative curve calculated
for thermogravimetric analysis data using a Savitsky-
Golay procedure.

DETAILED DESCRIPTION OF THE INVENTION

Hydrocarbon synthesis catalysts are generally
prepared by depositing a catalytic metal, usually

cobalt, upon a suitable support, e.g., a difficultly
reducible, porous, inorganic oxide, usually by contact-
ing the support by any of a number of known methods,
with a salt of cobalt. During the contacting step the
cobalt salt is impregnated onto the support. After
impregnation, the supported catalyst precursor is dried
to eliminate any excess solvent, that is, water by
virtue of using water soluble salts, or hydrocarbon
solvent by virtue of using hydrocarbon soluble com-
pounds. Drying can be accomplished with mild heating,
up to about 125°C in the presence of flowing gas
containing oxygen or hydrogen, either being optionally
diluted with an inert gas. When the drying gas con-
tains hydrogen, reduction does not occur at normal
drying temperatures and at the worst any reduction that
does occur will be insubstantial.

In some instances drying and reducing/
activating are accomplished in a single step by simply
raising the temperature when drying is substantially
complete. Nevertheless, at the onset of reduction,
whether one step drying/reducing or two step drying and
reducing is employed the catalyst precursor comprises a
reducible cobalt compound that forms water during
reduction of the precursor with hydrogen. A preferred
reducible cobalt compound is the oxide which is pre-
pared by treating the cobalt salt with an oxygen
containing gas, e.g., air, at temperatures of about
150°C to about 550°C for a period sufficient to convert
all or substantially all of the salt to the oxide.

Since the factors determining water partial
pressure during reducing/activating do not include the
nature of the support, this invention is applicable,
generally, to any of the known catalyst supports.

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Nevertheless, the support itself should be free of
water or water precursors to the extent that when
heated the support generates essentially no water
vapor. Typical supports include the oxides of metals
of Groups IIIA, IIIB, IVB, VB, VIB, VIIIB, mixtures
thereof, and mixtures thereof with other metal oxides,
e.g., alkali, alkaline earth metal oxides or rare earth
metal oxides. Preferred supports are those of lower
surface area, e.g., less than about 100 m^2/gm, prefer-
ably less than about 75 m^2/gm. Preferred materials are
the Group IVB metal oxides: zirconia, hafnia, and
titania as well as lower surface area aluminas, silicas
and silica-aluminas. Particularly preferred are the
Group IVB oxides, specifically titania, or a support
containing at least about 50 wt% titania, more prefer-
ably at least about 80 wt% titania.

When employing titania or a titania contain-
ing support, the rutile:anatase ratio is at least 2:3
as determined by x-ray diffraction (ASTM D 3720-78).
Preferably, the rutile:anatase ratio is at least about
3:2, more preferably at least about 4:1, an all rutile
titania is most preferred since high rutile content
titania provides a support wherein optional activity to
heavy hydrocarbons, e.g., $C_{10}+$, without significant gas
make, can be obtained.

The hydrocarbon synthesis catalyst is acti-
vated by reduction, which is carried out with hydrogen
or a hydrogen containing gas. The gas may be diluted
with an inert such as nitrogen, helium, or argon.
Other materials often considered inert such as CO or
CO_2 are not inert at these conditions and may either be
hydrogenated or result in carbon formation on the
catalyst.

In accordance with this invention, we have
found that the final temperature of the reduction has a
significant effect on the ultimate hydrocarbon synthe-
sis activity of the catalyst. In a preferred embodi-
ment of this invention, substantially complete reduc-
tion is effected at temperatures below about 550°C,
preferably from about 275°C to about 425°C and most
preferably, for maximizing catalytic activity, reduc-
tion is effected at temperatures ranging from 315°C to
about 375°C.

Temperature effects appear to be reversible,
whereas water partial pressure effects are apparently
irreversible. That is, incomplete reduction at rela-
tively low temperatures or over reductions at rela-
tively high temperatures, both of which lead to poor
catalytic activity, can be cured and catalyst activity
restored by, e.g., a 250°C air treat followed by a
satisfactory reduction step. Poor activity due to poor
control of the water partial pressure during reduction
cannot, however, be cured in this manner. The exact
mechanism affecting catalytic activity by virtue of
water partial pressures effects is unknown, neverthe-
less, the effect is clearly recognizable and can be
substantially eliminated by minimizing the water
partial pressure during reduction.

Reduction temperatures above 550°C are
generally not employed for reducing cobalt compounds
because of deleterious effects on catalytic activity.
Additionally, increasing the reduction temperature has
the effect of either causing the cobalt to agglomerate
or resulting in an SMSI (strong metal-support inter-
action) effect which causes a support overlayer to form
over the cobalt. In either case, the effective cobalt

surface area is significantly reduced and hydrocarbon
synthesis catalyst activity is deleteriously affected.
On the low end of the temperature scale, the cobalt
compound must be substantially reduced to obtain the
catalytically active form and thereby achieve reason-
able catalytic activity.

Referring to Figure 3, maximum reduction
temperature is plotted against relative catalyst
activity for catalyst B. Maximum activity increases
sharply at reduction temperatures of about 260°C and is
likely due to overcoming the reducing threshold of the
cobalt compound. Activity remains high and starts to
decrease at temperatures of about 400°C and more so
above about 425°C. These results were obtained at a
maximum water partial pressure of 0.24 atmospheres and,
therefore, represent maximum relative activity for this
particular catalyst.

The results for catalyst A are also plotted
in Figure 3 and show a decrease in relative catalytic
activity at reduction temperatures above about 370°C.

Also shown in Figure 3 is the XPS signal from
the catalyst surface. As the reduction temperature
increases above about 370°C for Catalyst B, the cobalt
signal declines relative to the titania signal suggest-
ing either that the cobalt is agglomerating or that a
titania overlayer is beginning to form on the cobalt
crystallites (a typical SMSI phenomenon). Either
mechanism results in reducing the exposed metal surface
area which is the parameter directly responsible for
catalytic activity.

The second and more important factor in the reduction step which has a significant effect on the ultimate activity of the catalyst is the maximum water partial pressure. Water is formed by the reduction reaction and can build up to significant partial pressures, depending on several factors. In accordance with this invention, the maximum water partial pressure is minimized to ensure optimum activity. Figure 2a shows that water partial pressures during reduction of greater than about 9 atmospheres cause a low activity, i.e., the curve becomes either flat or asymptotic at relative activity levels of about 70. In order to maintain high catalyst activity levels, water partial pressure should not exceed about 5 atmospheres. Stated another way, water partial pressure levels during reduction should be maintained at levels that furnish at least about 75% of maximum relative catalyst activity, preferably at least about 90% of maximum relative activity. In this manner, regardless of the maximum catalyst activity, which occurs at water partial pressures below about 1.5 atmospheres, the maximum water partial pressure that allows a certain level of catalyst activity can be predetermined.

The catalyst of this invention is useful in hydrocarbon synthesis reactions, that is, the catalytic conversion of synthesis gas, hydrogen and carbon monoxide, to higher hydrocarbons, preferably C_5+ hydrocarbons. The hydrocarbon synthesis process is carried out at temperatures of about 160°C to 325°C, preferably 190°C to 260°C, pressures of 5 atm to 100 atm (which also covers the activation pressures), preferably about 10-40 atm and gas hourly space velocities of 100 V/hr/V to 5000 V/hr/V, preferably 300 V/hr/V to 1500 V/hr/V. The stoichiometric ratio of

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hydrogen to carbon monoxide in the synthesis gas is
about 2.1/1 for the production of higher hydrocarbons.
However, H_2/CO ratios of 1/1 to about 4/1, preferably
about 1.5/1 to about 2.5/1, more preferably about 1.8/1
to 2.2/1 can be employed. These reaction conditions
are well known and particular reaction conditions will
be determined easily by those skilled in the art.
Also, the reaction may occur in any type reactor, e.g.,
fixed bed, fluidized bed, slurry bubble column, etc.

The catalysts employed in the practice of
this invention may be prepared by techniques known in
the art for the preparation of hydrocarbon synthesis
catalysts. The catalyst can, e.g., be prepared by
gellation, or cogellation techniques. Suitably however
the metals can be deposited on a previously pilled,
pelleted, beaded, extruded, or sieved support material
by the impregnation method. In preparing catalysts,
the metals are deposited from solution on the support
in preselected amounts to provide the desired absolute
amounts, and weight ratio of the metal or metals being
deposited. Suitably, cobalt by itself or with a
promoter are composited with the support by contacting
the support with a solution of a cobalt-containing
compound, or salt, or a promoter-containing compound,
or salt. Optionally, the cobalt and promoter can be
co-impregnated upon the support. The cobalt and
promoter compounds used in the impregnation can be any
organometallic or inorganic compounds which when
reduced in hydrogen form water or which can be con-
verted to the corresponding oxide, which when reduced
in hydrogen forms water., such as a cobalt or promoter,
nitrate, acetate, acetylacetonate, naphthenate, or the
like. The nitrate is preferred for cobalt. The amount
of impregnation solution used should be sufficient to

completely immerse the carrier, usually within the range from about 1 to 20 times of the carrier by volume, depending on the metal, or metals concentration in the impregnation solution. The impregnation treatment can be carried out under a wide range of conditions including ambient or elevated temperatures.

Promoter materials, such as rhenium, cerium, hafnium, and uranium can be included in the catalyst. Usually, these materials are present in a weight ratio to cobalt of at least about 0.05:1, preferably at least about 0.1:1 and may range from about 0.1:1 to 1:1, but the promoter is usually present in an amount less than the cobalt. Rhenium is a particularly preferred promoter and may be deposited onto the support as perrhenic acid. The amount of cobalt employed is at least that which is catalytically effective, e.g., at least about 2 wt%. However, cobalt concentrations may range from about 2-35 wt%, preferably 5-25 wt%.

The cobalt and promoter, e.g., rhenium, may be added serially although it is preferred to have the rhenium on the support before the cobalt is calcined. Or the metals may be simutaneously deposited onto the support.

In a preferred method for preparing the catalyst, cobalt or cobalt and one or more additional metals is deposited as a catalytically active layer, upon the peripheral or outside layer of a particulate porous inorganic oxide support by contacting the support and impregnating it with a liquid, suitably a suspension or solution, of a compound of said metal, or metals, while the support particles are in a fluidized bed maintained at a temperature above about 50°C,

preferably at a temperature ranging from about 50°C to
about 100°C, and more preferably from about 70°C to
about 90°C. The catalytically active surface layer,
ranges in average thickness from about 10 microns to
about 250 microns, preferably from about 20 microns to
about 200 microns, with the loading of the cobalt
expressed as the weight metallic cobalt per packed bulk
volume of catalyst ranging from at least about 0.04
grams per cubic centimeter preferably from about 0.05
g/cc to about 0.25 g/cc catalyst.

One preferred method for preparing catalysts,
either powdered or with particle size up to 3 or 4 mm
is disclosed in Preparation of Highly Selective and
Abrasion-Consistant Thick Shell Catalysts for Hetero-
geneously Catalyzed Exothermic Oxidation Reactions,
Arntz, D. and Prescher, G., Preparation of Catalysts
IV, Elsevier, Amsterdam, The Netherlands, p. 137-147
(1987).

The catalyst, after metal deposition, e.g.,
impregnation, is dried by heating at a temperature
above about 30°C, preferably between 30°C and 125°C, in
the presence of nitrogen, oxygen, hydrogen, or air, in
a gas stream or under vacuum. Subsequent to drying the
metal or metals may be converted to the oxide form and
then reduced/activated with a hydrogen or hydrogen
containing gas stream or the metal or metals may be
reduced/activated directly and the oxide formation is
eliminated. Preferably, however, the catalyst is
activated by reduction from the oxide form. Conversion
to the oxide takes place in air or an oxygen containing
stream at temperatures above about 150°C, preferably in
the range 150-550°C, more preferably about 150 to
300°C.

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Reduction/activation of the catalyst is effected in hydrogen or a hydrogen containing gas stream at temperatures above about 250°C, preferably from about 250°C to about 550°C, and more preferably from about 275°C to about 425°C, for periods ranging from about 0.5 to about 24 hours and at pressures ranging from above ambient to about 40 atmospheres.

Achieving maximum catalytic activity for any particular cobalt containing catalyst depends on several factors. We have already mentioned that reduction temperatures should not exceed about 550°C. Additionally, the water partial pressure during the reduction step should not exceed about 5 atmospheres and preferably should not exceed about 2.7 atmospheres.

Reactor vessels should be selected that avoid excessive buildup of water vapor. Thus, fluid beds are generally preferred where the hydrogen containing reducing gas fluidizes the catalyst particles. Reactors with high L/D ratios should be avoided.

Total pressure during the reduction/activation step is preferably above about 2 atmospheres and more preferably above about 5 atmospheres, more preferably above about 8 atmospheres. Total pressure is usually similar to the total pressure in a hydrocarbon synthesis reactor, i.e., about 8 to 100 atmospheres, preferably about 10-40 atmospheres.

Water partial pressure can be determined by direct measurement with available analytical devices, such as Drager tubes or suitable water analyzers manufactured for example by Manufacturers Engineering and Equipment Corp., Warrington, PA., or by

calculation. In calculating water partial pressure, the factors that affect water partial pressure are: total pressure; hydrogen and water concentrations in the reducing gas; total gas rate, e.g., space velocity; reactor type; rate of temperature increase, e.g., the ramp schedule; metal compound concentration.

Determination of water vapor partial pressure can be made by means of a model wherein the first consideration is the material balance for water vapor, which for any given (or predetermined) volume element of a reactor for a given (or predetermined) time period is expressed as (moles H_2O flowing into the volume element) + (moles water produced by reduction) = (moles water flowing out of the volume element) + (moles water accumulated in the volume element).

The material balance expression is easily formulated and solved for the particular reaction vessel being used.

This invention focuses on the moles of water produced by reduction in the volume element per unit time. For example, a hydrocarbon synthesis catalyst precursor containing cobalt oxide on a rutile titania support, gives rise to the following kinetic expressions to describe the rate at which water is produced in gram moles/minute/cc volume of reactor:

$$\frac{(\rho_{cat})\ (Co)\ (4)}{(3)\ (58.93)}\ \left(\ (0.25)\ \frac{d(y)_1}{dt} + 0.75\ \frac{d(y)_2}{dt}\ \right)$$

in which

ρ_{cat} is the catalyst bulk density, gm/cc

Co   is the weight fraction cobalt on dried, oxidized catalyst

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$\dfrac{d(y)_1}{dt}$ is the reduction rate of Co_3O_4 to CoO

$\dfrac{d(y)_2}{dt}$ is the reduction rate of CoO to metallic cobalt

The individual reaction rates can be further expressed for the reduction of Co_3O_4 to CoO:

$$\frac{d(y_1)}{dt} = (A_1)\ (F(Y_1))\ (F(T_1))\ (F(P_{H2}))\ (F(P_{H2O}))$$

and $\quad F(Y_1) = \dfrac{Y_1{}^{0.5}(1-Y_1)^{1.0}}{0.3849}$

$F(T_1) = EXP\ (-(13735/R)(1/T - 1/573.1))$

$F(P_{H2O}) = 1/1 + 3.803(P_{H2O})(EXP(4968/R)(1/T - 1/573.1))$

wherein Y_1 is the fraction Co_3O_4 reduced

       t is the reduction time in minutes

       A_1 is the pre-exponential for reaction (1) for a 12.15% Co catalyst and equals 0.62

     $F(Y_1)$ is the effect of extent of reduction on the reduction rate

     $F(T_1)$ is the effect of temperature on the reduction rate

       T is the absolute temperature in °K

       R is the gas constant, 1.987

    $F(P_{H2})$ is the effect of hydrogen partial pressure on reduction rate and is the hydrogen partial pressure in atm

    $F(P_{H2O})$ is the effect of water partial pressure on the reduction rate

Now, for the reaction CoO to metallic cobalt the kinetic expression is

$$\frac{d(Y_2)}{dt} = A_2\ (F(Y_2))\ (F(T_2))\ (F(P_{H2}))\ (F(P_{H2O})$$

wherein Y_2 is the fraction of metallic cobalt that has formed;

A_2 is the pre-exponential factor for the 12.15% catalyst and is 0.13

$F(Y_2)$ is the effect of the extent of formation of metallic cobalt on the formation rate and is $(Y_2)^{.7} (Y_1-Y_2)^{2.0}/0.2133$

$F(T_2)$ is the effect of temperature on the reduction rate and is
$EXP ((-18355/R) (1/T-1/573.1))$

T and R are as previously described

$F(P_{H2})$ is the effect of hydrogen partial pressure on the reduction rate and is the hydrogen partial pressure in atm

$F(PH_2O)$ is the effect of water partial pressure on the reduction rate and is

$$\frac{1-PH_2O/(14.344)(PH_2)(EXP (1086/T))}{1+3.803(PH_2O)(EXP(4968/R)(1/T-1/573.1))}$$

and t_2 is the reduction time in minutes

These rate expressions were developed with titania supported catalysts using thermogravimetric analysis techniques, and similar expressions were developed for alumina supported catalysts.

The kinetic model for the cobalt activation was developed from thermogravimetric analysis (TGA) data in which weights of the catalyst were measured periodically during reductions carried out at constant temperature. These weight data were then differentiated to obtain the rate of weight loss with time which is related to the reduction rate. Such isothermal data were obtained over a range of temperatures and reducing gas compositions (hydrogen, argon, and water vapor) to obtain measures of the effects of these variables on the reduction rate. Interpretation of the TGA data to

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develop the reduction model followed principles
proposed by Brown and Galwey (Brown, Michael E., and
Andrew K. Galwey). "Arrhenius Parameters for Solid-
State Reactions from Isothermal Rate-Time Curves."
Analytical Chemistry, Vol. 61, No. 10, May 15, 1989,
pp. 1136-1139).

In a typical TGA experiment, approximately
0.1 mg of the titania-supported cobalt catalyst was
charged to the balance pan of a Mettler Model TA-1
balance. Under a flow of 10 liters/minute of de-
oxygenated argon, the sample was heated to 500°C and
held at this temperature until constant weight was
achieved to remove adsorbed moisture. The temperature
was then lowered to a base temperature of 50°C to
obtain the weight loss by drying. Next, the sample was
reheated in argon to the temperature at which the
reduction experiment was to be conducted. At this
temperature, reducing gas of the desired composition
was introduced and the argon flow stopped. The reduc-
ing cycle was continued until constant weight was
achieved, after which temperature was again lowered to
the base temperature to determine the exact weight loss
due to reduction that had occurred. To validate the
experiment by assuring that no material had been blown
from the balance pan, the weight of the catalyst after
re-oxidation at 500°C was compared with the original
weight of the dried catalyst.

The weight data from the TGA experiment were
downloaded to a spreadsheet program in which the
derivative, or rate, data were calculated using the
numerical techniques developed by Savitzky and Golay
(Savitzky, Abraham and Marcel J. E. Golay. "Smoothing
and Differentiation of Data by Simplified Least Squares

Procedures." Analytical CHemistry, Vol. 36, No. 8, July 1964, pp. 1627-1639). The derivative curve calculated from the TGA data using the Savitzky-Golay procedure is shown in Figure 4.

The derivative curve in Figure 4 clearly shows two reduction peaks. The first corresponds to the reduction of Co_3O_4 to CoO while the second corresponds to the reduction of CoO to metallic cobalt. The dual peaks suggest that consecutive reactions are occurring and that the first reaction is nearly complete before the second reaction begins. The valley between the two peaks occurred after about one-fourth of the weight loss occurred, which also substantiates the concept of sequential reduction reactions. When reduction conditions of time and temperature were severe enough, the weight lost in the reduction agreed well with that expected if all of the Co_3O_4 were reduced to metallic cobalt.

Using the concepts of Brown and Galwey to interpret the nature of the reduction kinetics, the symmetry of each of the curves signals a sigmoid kinetic model rather than a deceleratory model. For a sigmoid kinetic model, the effect of the extent of reduction on the reduction rate can be represented mathematically by the following form:

$$F(y) = \frac{y^a * (1 - y)^b}{(a/(a+b))^a \, (b/(a+b))^b}$$

The coefficients a and b are chosen to fit the shape of the reduction curves, and the denominator normalizes the F(y) expression so that its values range between 0 and 1. The values at the peaks of the derivative

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curves in Figure 2 are proportional to the rate con-
stants for the two reduction reactions and can be
correlated directly with the independent variables of
temperature and reducing gas composition to develop the
reduction model.

To summarize the procedure of developing such
a reduction model, then, the following steps are used:

1)   Obtain isothermal reduction rate data by TGA for
      the range of temperatures, pressures, and reducing
      gas compositions of interest and calculate the
      derivative curves

2)   From the shapes of the derivative curves, select
      either the sigmoid or the decelaratory model as
      being more appropriate, and fit the appropriate
      mathematical form to the peaks

3)   Correlate the maximum of the derivative curves
      with the independent operating variables to obtain
      a mathematical relationship for their effects.

4)   These factors, combined with the stoichiometry of
      the reaction, can then be combined to obtain a
      comprehensive model of the reduction process.

*   The procedures described herein can be used, and
      modified as may be necessary, to determining water
      partial pressure effects for supports other than
      titania and reductions where water will be formed
      from the compound being reduced.

The following examples serve to illustrate
this invention.

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Two Co-Re-TiO$_2$ catalysts were prepared by impregnating an aqueous solution of cobalt nitrate and perrhenic acid onto titania extrudates. The extrudates contained about 3.5% alumina binder. Final calcination to decompose the nitrate salt was done in forced air ovens at 250°C. Catalyst extrudates were then ground and sized to 60-150 mesh for the activity tests and 60-100 mesh for the thermogravimetric (TGA) tests. The two catalysts differed in metal loading, as follows:

	Wt% Co	Wt% Re
Catalyst A	6.85	0.64
Catalyst B	12.15	1.23

The higher cobalt loading was deposited in two impregnation/calcination steps.

Catalyst tests were made in a small fixed bed reactor. A 1.2 cc (1.66 g) charge of catalyst was diluted with 1.2 cc of titania (also 60-150 mesh) and tested in a reactor with a 0.245 inch ID. The reactor was heated in an infrared furnace which permitted rapid changes in temperature. Reductions were performed with pure hydrogen metered with a Brooks flow controller. Gas hourly space velocities refer to the flow rate measured at the back-end of the unit with a bubble tube. Activity data, shown in Tables 1 and 2, correspond to performance at 18-22 hours on feed at 280 psig with a 64H2-32CO-4Ne feed composition. Run temperature was 200°C for Catalyst A and 190°C for Catalyst B. The rate constant k shown in the tables is calculated from the following equation:

$$k = (GHSV/P) \ln \left(1/(1-X)\right)$$

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where GHSV = vol gas flow (@ 1 atm and room
                  temperature) per hour per vol of
                  catalyst only
         P = pressure in atm = 20
         X = fraction CO conversion

Water was added during reduction via a metal saturator
or a Ruska pump. Levels shown in Tables 1 and 2
correspond to calculated values. Direct measurement by
Drager tube was unsuccessful because of condensation in
the exit line during water addition.

        Water concentration in the exit gas during
reduction was not routinely measured. However,
measurements were made in one side-by-side comparison
of the effect of flow rate alone. As shown in Figure
1, quite different concentration vs. time curves were
observed for 750 vs. 15,000 GHSV at 100 psig reduction
pressure. Water was removed much more slowly with the
lower flow rate. The high flow case is 67% more active
than the low flow case (see Table I). Other data in
Tables I and II confirm that reductions at elevated
pressure and low flow show consistently lower activity.
Data also indicate that this activity debit cannot be
eliminated by air regeneration. Water added after
reduction does not appear to be as harmful. Either dry
hydrogen or an air regeneration reverse the effect of
post-reduction water.

        Results from Tables I and II, taken under
conditions where water buildup was low, are illustrated
graphically in Figure 3. A maximum in activity occurs
after reduction at about 370°C. Higher temperature
reductions are especially poor. XPS results are
included in Figure 3. The ratio of the cobalt metal

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intensity to the Ti intensity shows a curve shaped like
the activity curves. The negative effect of high
temperature reduction appears reversible. Application
of a 250°C air treat to a 550°C reduced sample restores
high activity. This point is noted as the "X" on
Figure 3. XPS data indicate that the low activity
encountered with reductions below about 315°C is due to
incomplete reduction of the cobalt oxide.

The kinetics of cobalt reduction on titania
supported catalysts were developed from experiments in
which the rate of weight loss during reduction was
measured by thermogravimetric analysis (TGA). Kinetics
for other supports can be determined by similar
analyses. A Mettler Model TA-1 balance and the
Omnitherm software data-handling package were used to
make the kinetic measurements. The average particle
size for the catalysts was 50 microns, and material
smaller than 44 microns was removed by screening to
minimize the error due to fines being blown from the
sample holder. The range of conditions covered in the
kinetic study were as follows:

Temperature, °C	275 - 400
Total Pressure, Atm	1.0
Hydrogen Partial Pressure, Atm	0.19 - 1.0
Water Partial Pressure, Atm	0.0 - 0.29
Gas Flow Rate, L/Minute	5.0 - 10.0
Catalyst Cobalt Content, %	2.5 - 14.0

The reduction of the cobalt oxide to metallic
cobalt was found to occur in two sequential steps. In
the first step, Co_3O_4 was reduced to CoO; in the second
step, CoO was reduced to metallic cobalt. For each of
the two steps, the reduction rate was autocatalytic in
nature, i.e., the initial rate was low, then increased
as reduction took place to a maximum value before

falling off again as reduction for that step neared
completion. The reduction rate increased with tempera-
ture, was first order in both hydrogen partial pressure
and in the initial cobalt content of the catalyst, and
was inhibited by the presence of water vapor. Large
amounts of water vapor could also cause an equilibrium
limitation of the second reaction.

TABLE I

Catalyst A

Run No.	Temp °C	P, psig	GHSV	Time, hour	Comment	GHSV	% Co Conv	Mol% CH4	k
							200°C Run Data		
1	450	100	750	2		1250	73	3.6	82
2	450	100	15000	1		1750	79	4.5	137
3	450	100	750	2		1250	80	3.4	100
4	450	100	15000	1		1250	80	4.6	100
	450	100	15000	1	6% H2O				
5	450	100	15000	1		1750	74	4.6	118
	450	100	15000	4	4% H2O				
6	450	100	15000	1		1000	74	3.8	67
	450	100	15000	1					
	450	100	15000	1	23% H2O				
7	450	100	15000	1		1400	67	4.0	78
	450	100	15000	0.25					
	450	100	15000	1	23% H2O				
8	450	100	15000	1		1750	74	3.9	118
	450	100	3900	1					
	450	100	15000	1	23% H2O				
	250	0	4000	1					
	450	0	5000	1	5% O2/N2				

Activation Conditions *

* Heat-Up Rate = 20°C/Minute

TABLE I

Catalyst A

| Run No. | Activation Conditions * | | | | | 200°C Run Data | | | k |
	Temp °C	P, psig	GHSV	Time, hour	Comment	GHSV	% Co Conv	Mol% CH4	
9	450	100	750	2		1250	74	3.5	84
10	450	100	750	2		1500	72	3.6	95
	450	100	15000	1					
11	450	0	3000	1		1750	75	3.9	121
	450	0	3900	1	23% H2O				
	250	0	4000	1	5% O2/N2				
	450	0	5000	1					
12	450	100	750	2		1750	67	4.2	97
	250	0	4000	1	5% O2/N2				
	450	0	5000	1					
13	550	0	5000	1		1500	74	4.4	101
14	450	200	750	2		1000	74	3.5	67
15	371	0	5000	1		2250	69	5.1	132
16	450	300	750	2		1250	71	4.0	77

* Heat-Up Rate = 20°C/Minute

TABLE II

Catalyst B

Run No.	Heat-Up °C/Min.	Temp °C	Activation Conditions				190°C Run Data			
			P, psig	GHSV	Time, hour	Comment	GHSV	% Co Conv	Mol% CH4	k
1	20	371	35	300	1		1250	68	3.1	71
2	20	371	35	300	4		1500	72	3.0	95
3	20	400	0	5000	1		1875	70	4.5	113
4	20	375	0	5000	1		1875	70	4.8	113
5	1.67	375	35	300	3.5		1500	80	3.3	121
6	1.67	375	35	1200/750	2		1875	70	4.5	113
7	1.67	375	35	1200/750	2	5% H2O	1500	76	3.4	107
8	1.67	375	35	1200/750	2	6% H2O	2000	71	3.6	124
9	20	450	0	5000	1		1500	75	4.3	104
10	20	500	0	5000	1		1250	75	4.2	87
11	20	550	0	5000	1		1250	71	4.2	77
12	20	300	0	5000	1		1500	76	5.6	107
13	20	250	0	5000	1		500	64	3.9	26
14	20	275	0	5000	1		1500	74	4.4	101
15	20	550 250 375	0 0 0	1000 4000 5000	1 3 1	5% O2/N2	1750	70	4.2	1.05

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CLAIMS:

1. A method for preparing a cobalt containing hydrocarbon synthesis catalyst comprising

(a) preparing a catalyst precursor containing a reducible cobalt compound capable of producing water when treated with hydrogen at reducing conditions,

(b) substantially reducing the cobalt compound at elevated pressures and temperatures with a hydrogen containing gas, and

(c) maintaining the water partial pressure during step (b) below about 5 atmospheres.

2. The method of claim 1 wherein the total pressure during step (b) is above about 5 atmospheres.

3. The method of claim 1 wherein the temperature during step (b) is below about 550°C.

4. The method of claim 1 wherein the cobalt compound is cobalt oxide.

5. The method of claim 1 wherein the relative activity of the catalyst is at least about 75% of the maximum attainable catalyst activity for a particular catalyst composition.

6. The method of claim 1 wherein the cobalt is supported.

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7.   The method of claim 6 wherein the support
is selected from the oxides of Groups IIIA, IIIB, IVB,
VB, VIB, VIIIB, and mixtures thereof.

8.   The method of claim 7 wherein the support
surface area is less than 100 m^2/g.

9.   The method of claim 6 wherein the support
is a Group IVB metal oxide.

10.   The   method   of   claim   9   wherein   the
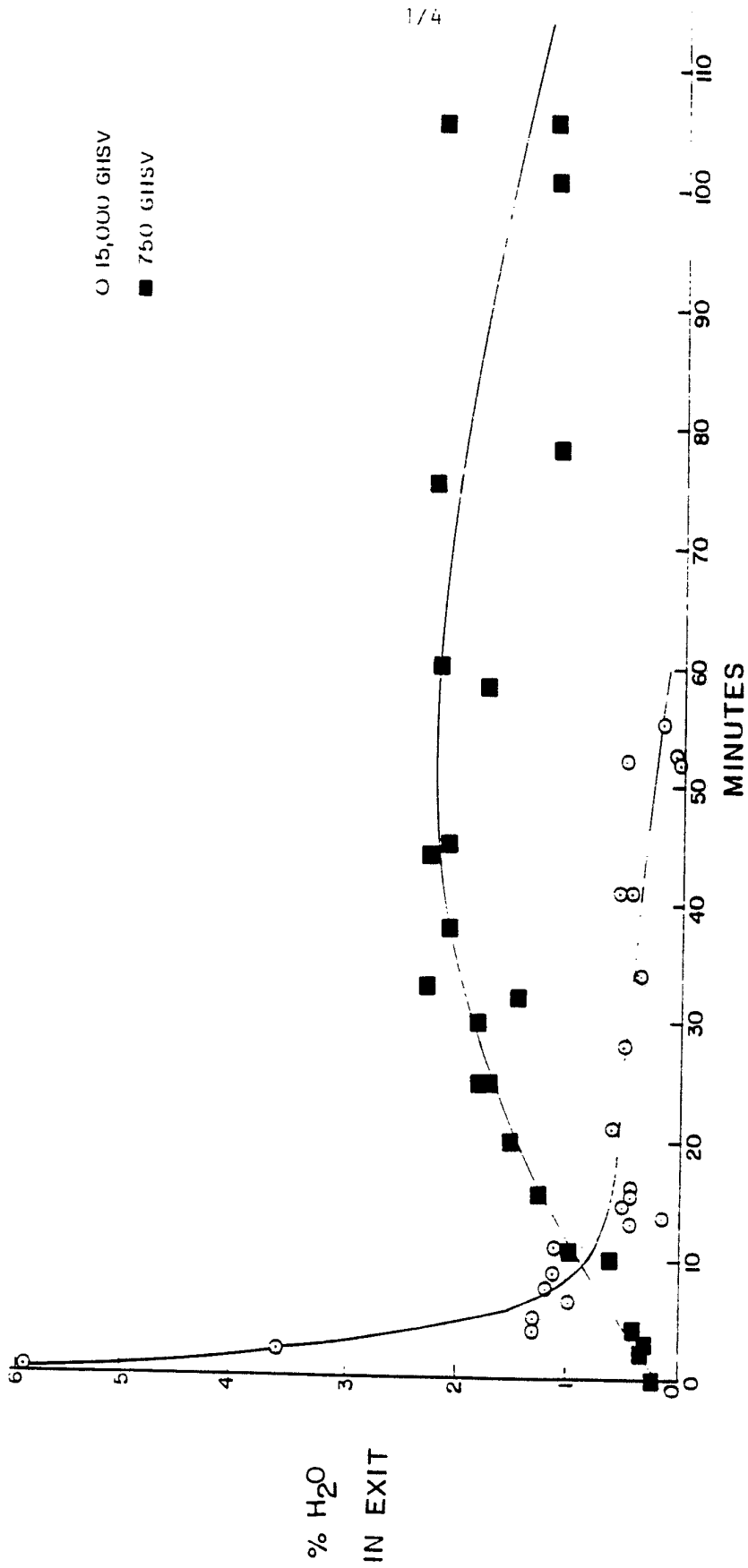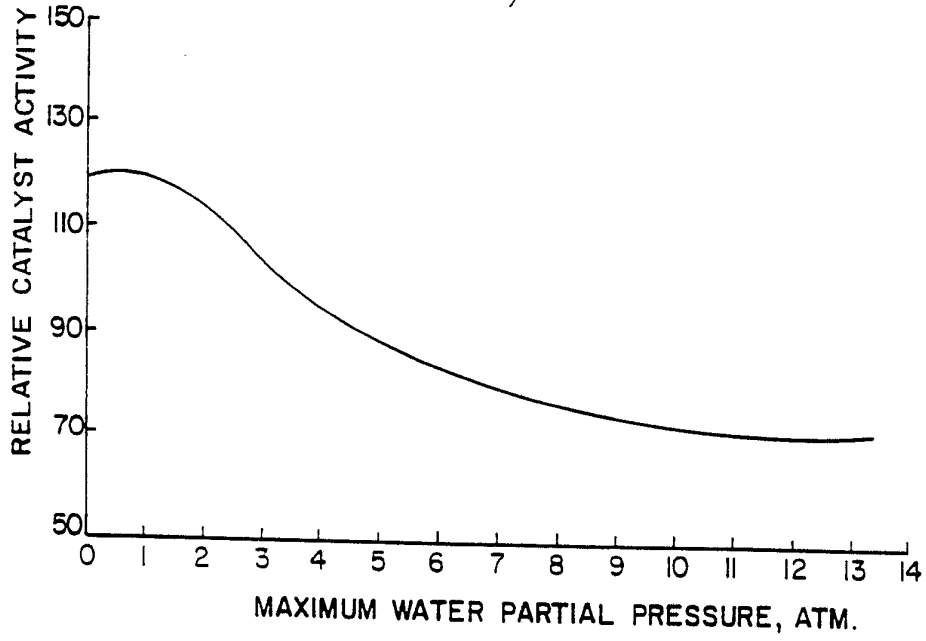support is titania.
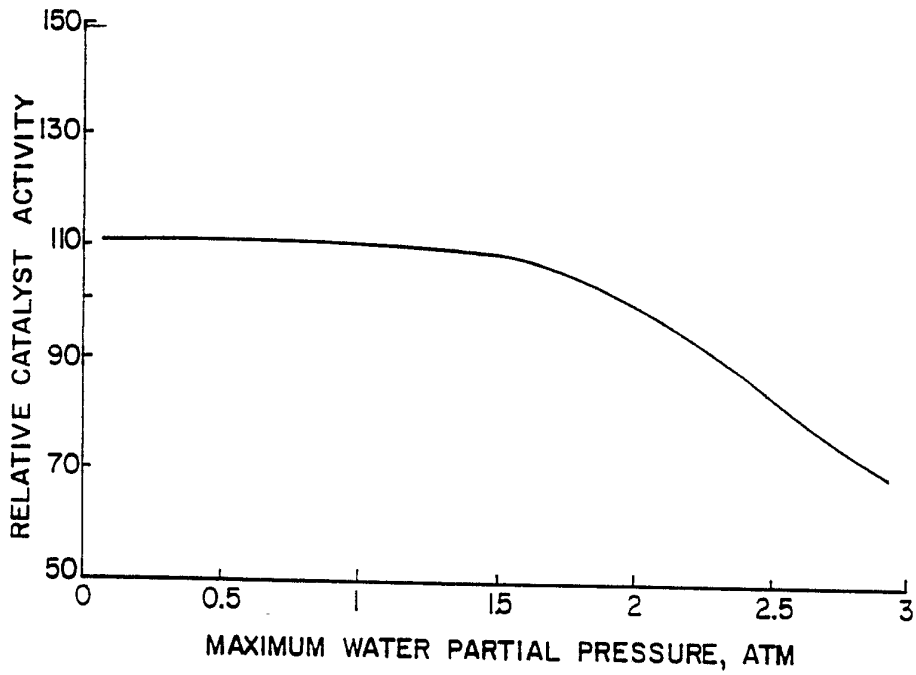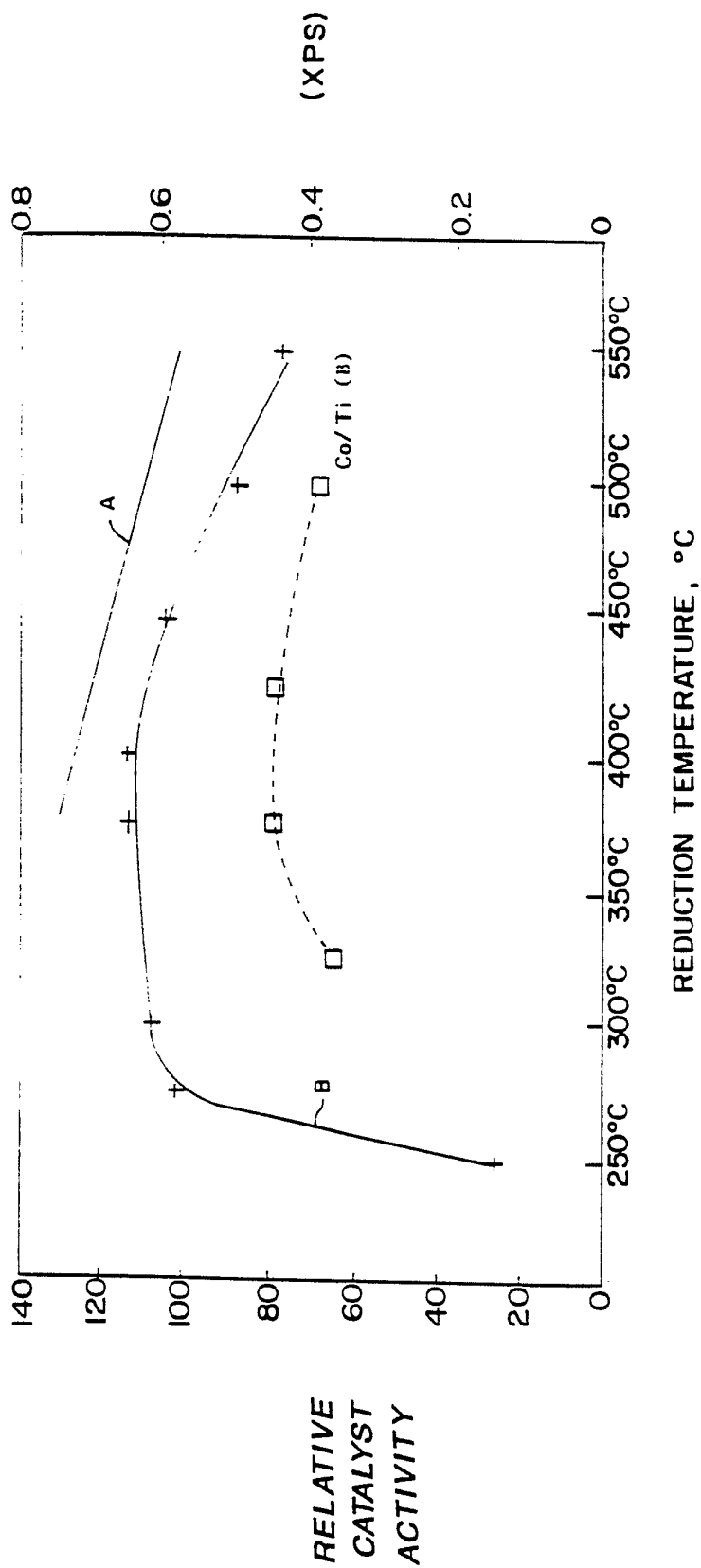
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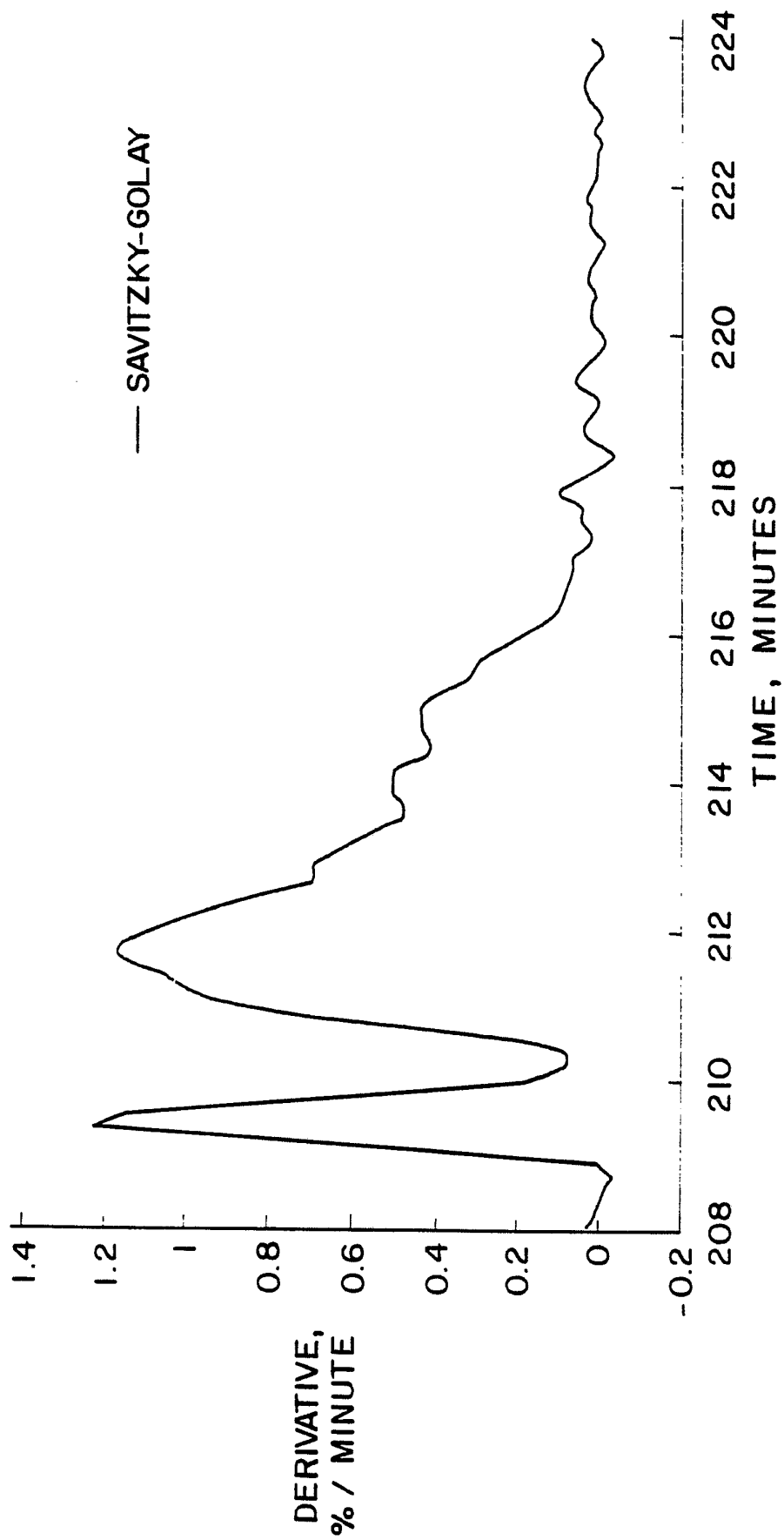

FIG. I

FIG. 2A

FIG. 2B

FIG. 3

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F I G. 4

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/07490

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

US 502/325,304,332

IPC(5):B01J 37/18,10; 21/06 .

II. FIELDS SEARCHED

Minimum Documentation Searched 7	
Classification System	Classification Symbols
US	502/325,304,332

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
X	US, A, 4,962,078 (BEHRMANN ET AL.) 09 OCTOBER 1990 Columns 4,5, and 8	1-10
X	US, A, 4,568,663 (MAULDIN) 04 FEBRUARY 1986 Columns 2,3,4, and 5.	1-10
X	US, A, 4,605,679 (KOBYLINSKI ET AL) 12 AUGUST 1986 Columns 1,2, 5 and 6.	1-10
A	US, A, 4,880,763 (ERI ET AL.) 14 NOVEMBER 1989	
A	US, A, 4,826,800 (MCATEER) 02 MAY 1989	

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03 DECEMBER 1991	3 0 DEC 1991

International Searching Authority	Signature of Authorized Officer
ISA/US	WILLIAM J. SHINE

Form PCT/ISA/210 (second sheet) (Rev.11-87)