AU-A-43791/85

88-091494/13 E17 H04 SHEL 15.05.85
SHELL INT RES MIJ BV *US 4729-981-A
02.06.86-US-869705 (+US-734189) *(08.03.88)* B01j-23/70
**Catalyst prepn. for converting synthesis gas to liq. hydrocarbon(s) - by impregnation or pptn. of cobalt or nickel on metal oxide support, and redn., oxidn. and redn.**
C88-041090

Div. ex: 4605676 (86-232207/35)
C.i.p.: 4585798 (86-081758/13)

Other Priorities: 11.10.83-US-540662 13.10.81-US-310969
02.06.86-US-869705 30.07.84-US-635911

Prepn. of a catalyst for conversion of syngas to a prod. contg liq. hydrocarbons comprises:

(A) depositing Co or Ni precursor on a refractory metal oxide support by impregnation or pptn., to distribute Co or Ni crystallites to form a supported catalyst; and

(B) activating the supported catalyst by subjecting it at about 100-450°C to (i) redn. in $H_2$, (ii) oxidn. in an $O_2$-contg gas, and (iii) redn. in $H_2$, to form an activated supported catalyst, more active for syngas conversion after step (iii) than after step (i).

The catalyst is also claimed.

E(10-J2D) H(4-E5, 4-F2, 4-F2E) N(2-B, 2-C, 5-B)

## ADVANTAGE

Steps B ('ROR activation') increase the catalyst's by up to about 100%.

## PREFERRED COMPONENTS

The support is pref. $SiO_2$ or esp. $Al_2O_3$. The catalyst pref. contains about 5-15wt.% Co. It may also contain a La or Mn promoter or about 0.05-0.50wt.% Ru.

## IMPREGNATION

Co may be impregnated onto the support using a non-aq. impregnating soln., esp. an acetone soln. The soln. may also contain Ru. E.g. the incipient wetness technique may be used.

## ACTIVATION

Steps (i) and (iii) are pref. conducted at about 200-450°C, and step (ii) at about 250-400°C. All 3 steps are pref. conducted while heating at about 0.1-2°C per min. The $H_2$ in steps (i) and (iii) may be mixed with $N_2$.

## EXAMPLE

A catalyst was prepd. by impregnating 22g $\gamma$-$Al_2O_3$ with 8.7g $Co_2(CO)_8$ in THF. It was activated by redn. in $H_2$, subjected to a synthesis run with CO and $H_2$ (1.85:1) at 195°C, and again activated by redn. with $H_2$, finally at 350°C for 1 hr. Its activity with syngas under the same conditions as before was then 1506cc CO reacted/g metal x hr. After further activating by oxidn. and redn. according to the invention, the activity of the catalyst, measured as before, was 1726cc CO/g metal x hr.(9pp1492CGDwgNo0/0)

87-170162/24 E36 H04 J04 KOBY/ 13.10.81
KOBYLINSKI T P *US 4670-414-A
20.06.86-US-876730 (+US-310977) *(02.06.87)* B01j-27/20

**Catalyst prepn. from cobalt carbonyl impregnated alumina or silica - by redn. in hydrogen oxidn. and redn. in hydrogen all below 500 deg. C giving improved syn-gas conversion**

C87-070900

Div. ex 4605679(86-232210/35)

Other priorities:
11.10.83-US-540662 30.07.84-US-635911 15.05.85-US-734188

Prepn. of a catalyst comprises activating a Co carbonyl-impregnated $Al_2O_3$ or $SiO_2$ support by (A) redn. in $H_2$, followed by (B) oxidn., and then (C) redn. in $H_2$, the temp. in this sequence being below 500°C.

USE/ADVANTAGE

The catalyst is useful for converting syngas to liq. hydrocarbons. If not promoted, its activity is nearly comparable with that of a conventional Ru-promoted catalyst made by impregnating Co nitrate on $Al_2O_3$; and it produces as much 5C+ hydrocarbons as do Ru-promoted Co catalysts which have been subjected to redn., oxidn. and redn. (ROR activation).

E(10-J2D3) H(4-E5, 4-F2E) J(4-E4) N(5-B, 6-E)

CATALYST PREPARATION

The Co carbonyl is pref. $Co_2(Co)_8$. The catalyst pref. contains about 3-20 (esp. 5-15)wt.% Co. It may also contain a La or Mn promoter. The activation steps are pref. conducted while heating at about 0.5-2°C per minute. Steps (A)-(C) are pref. conducted below about 450°C. A catalyst is pref. prepd. from extruded $\gamma$-$Al_2O_3$ by (i) impregnating with a non-aq. organic impregnating soln. contg. Co carbonyl and a Ru salt; (ii) redn. in $H_2$ at about 200-450°C; (iii) oxidn. at about 100-400°C; and (iv) redn. in $H_2$ at about 200-450°C.

EXAMPLE

22.0g $\gamma$-$Al_2O_3$, after acetone treatment and calcination at 300°C, was impregnated with 8.70g $Co_2(CO)_8$ in THF. The catalyst was first activated by heating at 5°C/min. in $H_2$ to 185°C; and holding there for 1 hr. It was then used for synthesis runs with syngas for 1 day at 185°C and then 1 day at 195°C; and then purged with $H_2$ at 185°C, heated at 1°C/min. to 350°C and held there for 1 hr. 2 further synthesis runs were then carried out as before. After then purging with $H_2$, and cooling under $N_2$, the catalyst was

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dosed with 6 pulses of an air/$N_2$ mixt. at room temp., and oxidised in flowing air while heating at 1°C/min. to 300°C and held there for 5.5 hr. After purging with $N_2$ and cooling, the catalyst was finally heated in $H_2$ at 1°C/min. to 350°C, and held there for 5.5 hr.(7pp1492RKMHDwgNo0/0)

US4670414-A

86-232210/35 E17 H04 J04 CALI 13.10.81
CHEVRON RESEARCH CO *US 4605-679-A
15.05.85-US-734188 (+US-310969) *(12.08.86)* C07c-01/04

**Synthesis gas conversion using activated cobalt catalyst - prepd. by impregnating alumina-silica support with di:cobalt octa:carbonyl in THF followed by reduction- oxidation-reduction**

C86-100028

Full Priorities: 13.10.81(2); 11.10.83; 30.07.84; 15.05.85-
-US-310969; 310977; 540662; 635911; 734188

Div ex. 4413864

C.i.p. 4493905

Synthesis gas is converted to liquid hydrocarbons using an activated, supported catalyst prepd. sequentially by

(a) impregnating an alumina or silica support with a cobalt carbonyl;

(b) activating the cobalt carbonyl by (i) reduction in hydrogen, (ii) oxidation with an oxygen-contg. gas, and (iii) reduction in hydrogen, the activating carried out below 450°C; and

(c) contacting a synthesis gas with the activated catalyst to form a product contg. liquid hydrocarbons.

E(10-J2D) H(4-E5, 4-F2E) J(4-E1, 4-E4) N(5-B)

ADVANTAGE

The activated cobalt carbonyl-impregnated catalyst provides very high reaction rates at moderate metal loadings, while at the same time, providing high selectivity, even without the use of the usual promoters.

EMBODIMENTS

The support is alumina. The cobalt carbonyl is $Co_2(CO)_8$. The oxidation step (ii) is carried out at 100°-400°C. The second reduction step (iii) is carried out at 100°-450°C. The activation steps are carried out at a heating rate of 0.5°-2.0°C per minute. The cobalt catalyst contains 1-30, pref. 3-20, esp. 5-15, wt.% cobalt.

The cobalt carbonyl-impregnated support is formed by impregnating the support with a non-aqueous organic solution of the cobalt carbonyl, wherein the solvent is tetrahydrofuran. The catalyst additionally contains 0.05-0.50 wt.% ruthenium. The catalyst consists of cobalt on alumina. The conversion process is carried out at 185°-250°C at 10-20 atmospheres. The support is silica. The catalyst additionally contains lanthanum or manganese promoter. (7pp1684RBHDwgNo.0/0).

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AU-A-43791/85

86-232207/35 E17 H04 CALI 13.10.81
CHEVRON RESEARCH CO *US 4605-676-A
15.05.85-US-734189 (+US-310969) *(12.08.86)* C07c-01/04
Redn.-oxidn.-redn. activated synthesis gas catalyst prepn. - from cobalt or nickel precursor on refractory metal oxide support, with ruthenium lanthanum or manganese promoters
C86-100025

E(10-J2D) H(4-E5, 4-F2E) N(2-B, 2-C)

C.i.p.: 4493905.

Full Priorities: 13.10.81(2); 11.10.83; 30.06.84; 15.03.85-US-310969, 310977, 540662, 635911, 734189.

Synthesis gas is converted to a prod. contg. liq. hydrocarbons using an activated. supported catalyst prepared by (a) depositing cobalt or nickel precursor on a refractory metal oxide support by impregnation or precipitation to distribute cobalt or nickel as crystallites; (b) activating the supported catalyst by (i) reduction in hydrogen, (ii) oxidation in an oxygen-containing gas, and (iii) reduction in hydrogen, all the steps carried out at 100-450°C; and (c) contacting synthesis gas under conversion conditions with the activated catalyst to form the prod.

**ADVANTAGE**

The activation procedure provides both promoted and unpromoted, supported cobalt and nickel catalysts with good reaction rates regardless whether the preparation was by impregnation or precipitation. The activation procedure can improve activity of promoted, supported cobalt and nickel catalysts, in which the promoter, such as ruthenium and lanthana have been previously added to improve activity.

**EMBODIMENTS**

The catalyst is prepared by subjecting cobalt on a refractory metal oxide support to the activation procedure. The catalyst is prepared by subjecting nickel on a refractory metal oxide support to the activation procedure. The support is alumina or silica, pref. alumina.

The temperature of step (a) is 200°-450°C, step (b) is 100°-400°C, and step (c) is 200°-450°C. The activation steps are carried out while heating at 0.1°-2.0°C per minute. The catalyst contains 5-15 wt.% cobalt.

The catalyst is prepared by impregnating the support with a non-aqueous, organic impregnation solution of cobalt salt prior to activation, in which the solution additionally contains a ruthenium salt and the non-aqueous solvent is acetone. The catalyst additionally contains 0.05-0.50 wt.% ruthenium, and may contain lanthanum or manganese promoters.

The catalyst consists essentially of cobalt on alumina.

The synthesis gas conversion process is carried out at 185°-250°C at 10-20 atmospheres pressure.

The support is silica.

The reducing gas used in step (i) is pure hydrogen or a hydrogen-nitrogen mixture.(9pp1684RKMHDwgNo0/0).

US4605676-A

AU-A-43791/85

86-081758/13 E17 H04 GULF 30.07.84
**GULF RESEARCH & DEV CO** *AU 8543-791-A
30.07.84-US-635911 *(06.02.86)* B01j-23/89 C01b-03/02

**Converting synthesis gas to liq. hydrocarbon(s) etc. by catalyst - contg. supported cobalt and ruthenium at molar ratio above 200:1 and pref. promoter oxide, showing acceleration by ruthenium**
C86-035073

Converting synthesis gas to a prod. contg. liq. hydrocarbons comprises contacting it under synthesis conversion conditions with a supported Co-Ru catalyst contg. about 5-30 wt.% Co and with a molar ratio Co:Ru of 200-3400:1. Other claims refer to an impregnation method for prepn. of the catalyst, and a method for its activation.

## ADVANTAGE

Although US4, 088, 671 discloses similar catalysts with Co;Ru molar ratios suitably up to 200:1, the present higher ratios can still give activities of at least twice those obtd. without Ru; and at higher pressure, Co:Ru ratios above 200:1 can give higher activities than ratios below 200:1.

## PREFERRED CATALYST

The support pref. comprises extruded gamma- or eta-$Al_2O_3$ or a mixt. thereof, and contains below 0.02 wt.% S.

E(10-J2D) H(4-E5, 4-F2E) N(2-B, 2-E)

The Co:Ru molar ratio is pref. 250-1000:1, esp. 300-700:1. The catalyst may also contain as promoter 0.1-5 wt.% of $La_2O_3$, $ThO_2$, MgO or a mixt. of rare earth oxides.

## CATALYST PREPARATION

Extruded $Al_2O_3$ calcined in air at 600-750° C, may be impregnated by the incipient wetness technique with a non-aq. soln. of Co and Ru cpds., pref. $Co(NO_3)_2$ or $Co_2(CO)_8$ and Ru acetylacetonate, opt. with a promoter metal salt, e.g. $La(NO_3)_3$. The pref. solvent is acetone, when using $Co(NO_3)_2$ or THF when using $Co_2(CO)_8$. There may be several impregnations, with slow drying and calcinations (pref. to 250-300° C) after each. The catalyst is finally activated by redn. in $H_2$ at 200-450° C, oxidn. at 100-400° C, and final redn. in $H_2$ at 200-450° C: during activation the catalyst may be heated at 0.5-2° C per min.

## PROCESS

The synthesis gas is pref. reacted at at least 3.4 (esp. about 13-20) atmospheres, 185-250° C and GHSV 1000-2500.

**EXAMPLE**

Catalysts were prepd. as described above using $Co(NO_3)_2$ as the source of Co, and activated by a single $H_2$ treatment. They comprised gamma-$Al_2O_3$, with (wt.%) (A) 20.0 Co, 1.00 $La_2O_3$ and 0.05 Ru (Co/Ru = 693 molar) and (B) the same as (A), but omitting Ru. A mixt. of $H_2$ and CO (2:1) was passed over the catalyst at 14 atmosoheres, 195°C and 1749 cc/g x hr. The CO conversion rate (cc/g x hr) was (A) 336, (B) 86. (25pp1492RKMHDwgNo 0/0).