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E17 H04

ESSO 29.08.88

EXXON RES &amp; ENG CO

\*US 4960-801-A

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**Prodn. of C5 hydrocarbon(s) via synthesis reaction - with a catalyst comprising cobalt on a titania support containing silica C90-138461**

C5+ hydrocarbons are prep'd. by reacting hydrogen and carbon monoxide in the presence of a catalyst (I) comprising:

- cobalt in a catalytically active amt., and
- an inorganic refractory support, comprising a major portion of titania, to which up to 15 wt.% of silica, in the form of silica or a silica precursor has been added.

ADVANTAGE

(I) is more active for CO conversion than catalysts not containing silica, and allows reduced operating temp. with consequent decrease in selectivity to methane and increase in C5+ yield.

PREFERRED CATALYST

(I) contains 5-20 wt.% Co, opt. with a promotor metal, esp. rhenium in Re:Co wt. ratio 0.025-0.1:1. Silica is 1-10, esp. 3-7 wt.%. The titania has rutile:anatase ratio 4:1 to

E(10-J2D3) H(4-E5, 4-F2E) N(1-D, 2-B, 3-B)

100:1, or is 100% rutile; surface area of the support is less than 50 m<sup>2</sup>/g.

The catalyst may be prep'd. by gelation or cogellation techniques, or esp. by depositing the metals on a previously pilled, pelleted, beaded, extruded or sieved support material by a conventional impregnation method followed by oxidation with an oxygen-containing gas.

REACTION CONDITIONS

Reaction pref. takes place at 160-300°C, H<sub>2</sub>:CO ratio 0.5:1 to 10:1, GHSV 100-5000.

EXAMPLE

Cobalt and rhenium were deposited from acetone solution onto calcined TiO<sub>2</sub> (rutile 97%, surface area 14 m<sup>2</sup>/g) using a slurry technique. The slurry was dried, calcined at 250°C, and screened to remove fines. SiO<sub>2</sub> was deposited onto the product by incipient wetness impregnation with a solution of tetraethoxysilane in methanol in an inert atmosphere, followed by decomposition of the silane by treatment with water-saturated He at 25-400°C. The product was reduced with hydrogen at 450°C to obtain a

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catalyst containing 11 wt. % Co, 0.4 wt. % Re and 5.2 wt. % SiO<sub>2</sub>.

A 2/1 H<sub>2</sub>/CO mixture was passed over the catalyst at 200°C, 2050 kPa. At 119 hr. on stream, volumetric productivity was 410 (295) cc CO converted/cc catalyst/hr., and selectivity to C<sub>5</sub>+ hydrocarbons 89.1% (89.9%). Figures in brackets are for a catalyst prepd. with omission of the SiO<sub>2</sub> deposition step. (8pp1644SLDwgNo0/2).

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Hydrocarbon synthesis catalyst comprising cobalt on support -  
contg. titania, and minor amt. of silica giving higher productivity

C89-010540

Hydrocarbon synthesis catalyst comprises Co in catalytically active amt. composited with an inorganic refractory support consisting of  $TiO_2$  to which up to 15 (e.g. 3-7) wt. %  $SiO_2$ , in the form of  $SiO_2$  or a precursor has been added.

USE/ADVANTAGE

The catalyst is useful in the prodn. of hydrocarbons from  $H_2$  and CO. The added  $SiO_2$  increases the activity, either as Co-time yield or as Co site-time yield, by pref. more than 40% (esp. more than 50%). The synthesis temp. can then be reduced and the  $CH_4$  selectivity thereby reduced and the  $5C^+$  yield increased. Carburisation of the catalyst is drastically inhibited.

PREFERRED COMPONENTS

The  $TiO_2$  may have a rutile:anatase ratio of at least 2:3, or esp. may be 100% rutile. Re in catalytic amt. and Th may

E(10-J2D) H(4-E5, 4-F2E) N(1-D, 2-B1, 3-A, 3-B, 3-E, 6-E)

also be present.

PREPARATION

The  $SiO_2$  or its precursor may be added to the support before or after the incorporation of the Co. E.g. a CoRe/ $TiO_2$  catalyst may be  $SiO_2$  promoted by incipient wetness impregnation with a soln. of tetraethoxysilane (TEOS) in MeOH, followed by treatment with  $H_2O$ -sald. He at up to  $400^\circ C$  to decompose the TEOS.

EXAMPLE

A prior art catalyst (A) contained (wt. %) about 11.6 Co and 0.46 Re on  $TiO_2$  (97% rutile), and a catalyst of the invention in addn. contd. 5.2  $SiO_2$ , introduced as above. Both were steamed.  $H_2$  and CO (2:1) were reacted at  $200^\circ C$ , 2100 kPa and about 60% CO conversion. After 190 and 119 hrs respectively, the volumetric productivity (cc converted/cc CAT. hr) was (A) 240, (B) 410. (8pp1492CGDwgNo/2)