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 EXXON RES & ENG CO \*US 4567-205-A  
 20.05.85-US-734783 (+ US-626024) (28.01.86) C07c-01/04  
 Adding rhenium to fischer-tropsch catalyst of ruthenium on titania - reduces deactivation rate while maintaining high selectivity to straight-chain middle-distillate hydrocarbon(s)  
 C86-020369

Process for hydrocarbon synthesis from a mixt. of CO and H<sub>2</sub> comprises contacting it with a catalyst comprising (i) Ru (1 proportion by wt.) composited with (ii) a TiO<sub>2</sub> or TiO<sub>2</sub>-contg. support, having a rutile/anatase ratio of at least about 2:3, and (iii) Re (0.25-2 proportions by wt.) in amt. sufficient to improve the maintenance of catalytic activity.

#### USE/ADVANTAGE

High quality middle distillate fuels are produced, consisting of mixts. of linear paraffins and olefins. The known good performance of Ru/TiO<sub>2</sub> catalysts, including high activity and low CH<sub>4</sub> and CO<sub>2</sub> selectivities (see US4042614), is maintained, but the rate of activity loss is reduced.

#### PREFERRED CATALYST

The rutile/anatase ratio of the support is about 2:3 to 100:1; and the catalyst contains 0.01-8 (esp. 0.2-4) wt. % Ru

E(10-J2C3, 10-J2D) H(4-E5, 4-F2E) N(2-E, 3-B, 3-E)

and 0.01-8 (esp. 0.1-4) wt. % Re.

#### CATALYST PREPARATION

The catalyst is prepd. from a pilled, pelleted, beaded, extruded or sieved TiO<sub>2</sub> support impregnated with Ru and Re salts from soln., together or sequentially, and the prod. then dried at 65-150 deg. C. and reduced (e.g. by H<sub>2</sub> and opt. CO) at 150-500 deg. C and 100-4000 kPa for 0.5-24 hrs.

#### PROCESS

The H<sub>2</sub>/CO mixt. is pref. contacted with the catalyst at a mole ratio of 0.1-10:1 (esp. 0.5-4:1), GHSV 100-20,000 (esp. 300-2,000), temp. 150-500 (esp. 180-300) deg. C. and pressure 100-100,000 (esp. 100-3,100) kPa. The prod. generally contains 60% (pref. at least 75%) 10C+ liq. hydrocarbons.

#### EXAMPLE

H<sub>2</sub> and CO (2:1) were reacted at 280 psig, 230 deg. C and GHSV 1000 over catalysts (A) (following the invention), comprising 1% Ru/0.5% Re/TiO<sub>2</sub>; and (B) (comparative), comprising 1% Ru/TiO<sub>2</sub>. Initially the total CO conversion was (A) 97%, (B) 97%; and CO conversion to hydrocarbons was (A) 90%, (B) 94%. The half-life of the conversion to hydrocarbons was (A) 231 days, (B) 26 days. (5pp1492RHDwgNo 0/0)