85-248995/40 H04 ESSO 29.06.84
EXXON RES & ENG CO *US 4542-122-A
29 06 84-US-626013 (17.09.85) B01j-21/06 B01j-23/74

Thoria promoted cobalt catalyst yielding higher hydrocarbon - from methanol and from synthesis gas in high yields with high selectivity and activity without excessive carbon dioxide

C85-108016

Catalyst composition for the conversion of methanol or synethesis gas to hydrocarbons consists of cobalt, or cobalt and thoria in catalytically active amount composited with titania or a titania-containing support, wherein the titania support is one having a rutile:anastase ratio of at least 2:3.

ADVANTAGE

A catalyst for the conversion of methanol, and synthesis gas respectively, at high conversion levels, and at high yields to premium grade transportation fuels, especially C10+ distillate fuels; particularly without the production of excessive amounts of carbon dioxide.

PREFERRED EMBODIMENTS

A more selective catalyst for methanol conversion reactions is one containing titania wherein the rutile:anastase ratio is 2:3 to 3:2. In its preferred form the titania, or titania component of the carrier, or support, when used in the conversion of synthesis gas will generally contain a rutile:anastase ratio of at least 3:2, generally from 3:2 to 100:1 or greater, and more preferably from 4:1 to 100:1 or greater. The cobalt, or cobalt and thoria, is dispersed on the support in catalytically effective amounts. In methanol conversion reactions the use of thoria with the cobalt is particularly preferred.

In terms of absolute concentration, suitably, the cobalt is dispersed on the support in amount of 2-25, pref. 5-15, percent, based on the total weight of the catalyst composition (dry basis). The thoria is dispersed on the support in amounts of 0.1-10, pref. 0.5-5, percent, based on the total weight of the catalyst composition (dry basis). Suitably the thoria promoted cobalt catalyst contains cobalt and thoria in ratio of 20:1 to 1:1, pref. 15:1 to 2:1, based on the weight of the total amount of cobalt and thoria contained on the catalyst. These catalyst compositions produce at reaction conditions a product which is predominantly C10+ linear paraffins and olefins, with very little oxygenates.

METHANOL CONVERSION

The partial pressure of methanol within the reaction mixture is above 100, pref. above 200, psin. Methanol, with added hydrogen are employed in the molar ratio above 4:1, pref. above 8:1 to increase the concentration of C10+ hydrocarbons in the product. Suitably, the methanol:hydrogen molar ratio, where hydrogen is employed, ranges from 4:1 to 60:1, pref. 8:1 to 30:1. Inlet hydrogen partial pressures are pref. below 80, and more pref. below 40, psin; inlet hydrogen partial pressures pref. range from 5-80, more pref. 10-40, psia. In general, the reaction is carried out at liquid hourly space velocities of 0.1-10, pref. 0.2-2, per hour, and at temperatures of 150-350, pref. 180 250, deg. C. Methanol partial pressures pref. are 100-1000, more pref. 200-700, psin. The product pref. contains over 60, more pref. over 75, percent C10+ liquid hydrocarbons which boil above 160 deg. C.

SYNTHESIS GAS REACTIONS

The total pressure upon the reaction mixture is maintained above 80, pref. above 140, psig, and employs hydrogen:carbon monoxide in molar ratio above 0.5:1, pref. equal to or above 2:1 to increase the concentration of C10+ hydrocarbons in the product. Suitably, the hydrogen:carbon monoxide molar ratio is 0.5:1 to 4:1, pref. 2:2 to 3:1. The reacton is carried out at gas hourly space velocities of 100-5000, pref. 300-1500, V/Hr/V, and at temperatures of 160-290, pref. 190-260, deg. C. Pressures pref. are 80-600, more pref. 140-400, psig. The product pref. contains over 60, more pref. over 75, percent C10+ liquid hydrocarbons which boil above 160 deg. C. (9pp1684RHDwgNo0/0)

US4542122-A