90-178370/23 E33 H04 J04 ESSO 18.12.87
EXXON RES & ENG CO *US 4923-841-A
13.12.88-US-283690 (+US-134796) (08.05.90) B01j-27/12

Particulate fluorided GP = VIII metal-on-alumina catalyst - useful for hydro-treating wax to obtain liq. fuel

C90-077470

A novel particulate fluorided Group VIII metal-on-alumina catalyst (I) has

(a) a Gp. VIII metal concn. 0.1-2 wt. %; the metal is esp. Pt;

(b) a bulk fluoride concn. 2-10 (5-8) wt. %; the fluoride concn. is less than 3.0 (0.5) wt. % at the outer surface to a depth of iess than 0.01 in.; the surface fluoride concn. is less than the bulk fluoride concn.;

(c) an aluminium fluoride hydroxide hydrate (II) level greater than 60 (100), where 100 corresponds to the X-ray diffraction peak height at 5.66Å for a reference standard; and

(d) a N/Al ratio less than 0.005 (0.002).

Prepn. of (I) is also claimed.

E(10-J2D) H(4-B3, 4-E, 4-E8, 4-F2B, 4-F2E) J(4-E4)

USE

(I) is of use for producing liq. hydrocarbon fuels from wax, esp. middle distillate hydrocarbons with low freezing point and high diesel cetane index by hydroisomerising and hydrocracking a Fischer-Tropsch wax.

PREPARATION

Catalyst (I), in which the metal is Pt, is prepd. by:
(i) contacting a calcined platinum-on-alumina catalyst with an aq. solution contg. 10-20% HF and having pH below 3.5 to distribute fluoride within the alumina; a distinct inner ring of fluoride is formed; and
(ii) drying at a temp. not more than 650 deg. F.

EXAMPLE

A precalcined commercial reforming catalyst (Ketjen CK-306, (RTM) in the form of 1/16 in.dia. extrudates was covered with an 11.6 wt. % HF solution for six hours, the solution decanted and the catalyst washed, dried at up to 260 deg. F and then reduced by contact with hydrogen at 650 deg. F; average pore dia. was 100-150 Å, pore vol. 0.5-0.6 cc/g, surface area 121.8 m^2/g. A major part of the fluoride was present as (II).

This catalyst was used for hydrotreatment at 650 deg. F. 1,000 psi, of a 550 deg. F + fraction of Fischer-Tropsch wax. A liq. prod. of pour point 21 deg. F was obtained. A comparison catalyst which was calcined at 1000 deg. F before the hydrogen reduction,and did not contain a significant amt. of (II),gave a prod. of pour point 75 deg. F.(16pp1644CGDwgNo0/5).

US4923841-A

89-180134/25 H04 (H06) ESSO 18.12.87
EXXON RES & ENG CO *EP -321-301-A
18.12.87-US-134796 (21.06.89) B01j-23/40 B01j-37/26 C10g-45/62 C10g-47/14

Particulate catalyst for producing liq. hydrocarbon from wax - comprising Gp=VIII metal on fluorided alumina with specified distribution of fluorine

C89-079542 R(DE FR GB IT NL)

A particulate fluorided metal-on-Al_2O_3 catalyst has (a) 0.1-2 wt.% of a Gp. VIII metal, (b) bulk fluoride concn. 2-10 wt., and less than 3% in the outer surface layer to a depth of less than 0.254 mm, with the surface fluoride concn. less than the bulk fluoride concn. (c) an Al fluoride hydroxide hydrate level about 60, where a level of 100 corresponds to the X-ray diffracton peak at 0.566 nm for a Reference Standard, and (d) N/Al ratio less than 0.005 (e.g. less than 0.002).

USE

The catalyst is used in prodn. of liq. hydrocarbon fuels from wax, esp. in hydro-isomerising and -cracking a Fischer-Tropsch wax to liq. hydrocarbon, esp. to more valuable mid distillate hydrocarbons with low f.pt. and high diesel cetane index.

H(4-A7, 4-B3, 4-D3, 4-F2A, 4-F2B, 4-F2D) N(1-C2, 2, 4-D, 6-E)

PREFERRED CATALYST

The metal is Pt, the Al fluoride hydroxide hydrate level is at least 80 (e.g. at least 100), the surface fluoride concn. is less than 1 (e.g. less than 0.5) wt. %, and the fluoride concn. is 5-8 wt.% w.r.t. total catalyst.

PREPARATION

(a) A calcined Pt-on-Al_2O_3 compsn. with 0.1-2 wt. % Pt is contacted with a HF soln. with pH below 3.5 (pref. an aq. soln. contg. 10-20% HF), to distribute fluoride within the interior of the Al_2O_3 and to give a compsn. contg. 2-10% fluoride, with a distinct inner ring of fluoride, (b) the compsn. is dried at not above 343.3 deg. C (e.g. not above 148.9 deg. C), and (c) the catalyst, pref. with Al fluoride hydroxide hydrate level of at least 100, is recovered.

EXAMPLE

(I) A 1/16 inch extrudate of "Ketjen" CK-306 (RTM: precalcined reforming catalyst) was contacted with 11.6% HF soln. washed, dried in flowing air, and then at 260 deg. F. (A) The catalyst was reduced in H_2 at 650 deg. F, giving a catalyst with pore dia. 100-150 Å, pore vol. 0.5-0.6 cc/g,

surface area 121.8 m^2/g, 1.4% F at the edge, and most of the fluoride present as Al fluoride hydroxide hydrate. Or, (B) the catalyst was calcined at 1000 deg. F, and reduced in H_2 at 650 deg. F, giving a catalyst with pore dia. 175 Å and surface area 165.1 m^2/g. Both catalysts contained 0.58% Pt and 7.2% F.

(II) Each catalyst was crushed to 14/35 mesh and used to hydrocrack and hydroisomerise a 550+ deg. F fraction split from a raw Fischer-Tropsch wax (hard solid, API gravity 39.0). Reaction was at 660 deg. F, 1000 psi, space velocity 0.5 vols./vol./h, and gas rate 8000 SCF H_2/B.

Properties of the prods. were: API gravity, (A) 44.8, (B) 42.6; pour point, deg. F, (A) 21, (B) (75).
(18pp510CGDwgNo0/4).
(E) ISR: No Search Report.