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 EXXON RES & ENG CO \*US 4959-337-A  
 13.12.88-US-283709 (+US-134795) (25.09.90) B01j-21/04  
 B01j-27/12  
**Wax isomerisation catalyst of high activity and selectivity -  
 comprising hydrogenation metal on a fluorided alumina support  
 C90-135094**

A novel wax isomerisation catalyst (1) comprising a Gp. VIII hydrogenation metal component on fluorided alumina, or material contg. alumina support comprises:

- (a) a surface nitrogen content as determined by X-ray photoelectron spectroscopy of 0.01 N/Al or less;
- (b) bulk F content of 2 - 10 wt. %;
- (c) surface F content (the amt. of F in a layer extending about 0.01 in. from the surface) less than 3 wt. % and less than the bulk F content; and
- (d) aluminium fluoride hydroxide peak height of 60 or less, determined as the relative amt. of hydrate represented by a peak in the X-ray diffraction pattern at  $2\theta = 5.66 \text{ \AA}$ , when a hydrate level of 100 corresponds to the peak height exhibited by a standard material. The standard material is a Pt on fluorided alumina containing 0.6 wt. % Pt on  $150 \text{ m}^2/\text{g}$  surface area alumina fluorided using an aq. soln. contg. a

H(4-A10, 4-F2A) N(2)

high concn. of HF to deposit 7.2 wt. % F on catalyst and dried at  $150^\circ\text{C}$  for 16 hr.

Prodn. of (1) is also claimed.

#### USE/ADVANTAGE

(1) is of use for conversion of waxes to lube oil base stock or blending stock. It has both high activity and high selectivity, properties not usually found together in the same material.

#### PREFERRED COMPOSITION

Pref. the hydrate level of (1) is 10 - 60, and the N/Al ratio 0.007 or less. The hydrogenation metal is a noble metal, esp. Pt, forming 0.1 - 5 wt. % of the catalyst.

The support is  $\gamma$  or eta alumina.

Bulk fluorine content is 5 - 8 wt. %.

#### PREFERRED PROCESS

The hydrogenation metal is deposited on the support, and the loaded support calcined, fluorided using a fluorine source of pH 3.5 - 4.5 to a bulk fluorine level of 8 wt. % or less (or using a fluorine source of pH less than 3.5 to a bulk

fluorine content of 10 wt. % or less), and heated to 350 - 450°C in air, oxygen-containing atmosphere, hydrogen or inert gas. The product may be activated by heating in a hydrogen-containing atmosphere at 350 - 500°C.

EXAMPLE

A commercial catalyst consisting of 1/16 in  $\gamma$  alumina extrudates containing 0.6 wt. % Pt and ca. 1 wt. % chlorine was fluorided using a solution of  $\text{NH}_4\text{F}/\text{HF}$  of pH 4, dried, calcined at 400°C, and activated in hydrogen. N/Al ratio was 0.0037, hydrate level 29, F (bulk) 6.9 wt. %, F (surface) 1.7 wt. %.

The high activity and selectivity of this catalyst when used with a 600 N slack wax feed was attributed to the uneven fluorine distribution. (21pp1644SLDwgNo0/0).

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 EXXON RES & ENG CO

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Wax isomerisation catalyst - comprising hydrogenation metal on fluorided alumina support with specified distribution of fluorine  
 C89-079541 R(BE DE ES FR GB IT NL)

A wax isomerisation catalyst comprising a Gp. VIII hydrogenation metal component on a fluorided support of, or contg.  $Al_2O_3$ , has a surface N/Al ratio, determined by X-ray photoelectron spectroscopy, not above 0.01 N/Al, bulk F content of 10-12 wt. %, F content in the layer between the outer surface and extending 0.254 mm in from the surface of less than 3%, with the surface fluoride concn. less than the bulk fluoride concn., and an Al fluoride hydroxide hydrate peak concn. of not above 60, determined as the relative amt. of hydrate represented by a peak in the X-ray diffraction (XRD) pattern at  $2\theta = 0.566$  nm when a hydrate level of 100 corresponds to the XRD peak height of a standard material which is a Pt on fluorided  $\gamma-Al_2O_3$  contg. 0.6% Pt on  $Al_2O_3$  with surface area 150  $m^2/g$ , fluorided in conc. aq. HF to deposit 7.2% F, and dried at 150 deg. C for 16 h.

H(4-A7, 4-E, 4-F2A, 4-F2E) N(1-C2, 2, 4-D, 6-E)

#### ADVANTAGE

The catalyst has high activity and selectivity in conversion of wax to lubricant oil base stock or blending stock.

#### PREFERRED CATALYST

The hydrate level is 10-60, the N/Al ratio is not above 0.007, the metal is a noble Gp. VIII metal, e.g. Pt, in amt. of 0.1-5 (e.g. 0.1-1) wt. %, and the bulk F content is 5-8 wt. %.

#### PREPARATION

A Gp. VIII hydrogenation metal is deposited on a  $Al_2O_3$  support (pref.  $\gamma$ - or eta- $Al_2O_3$ ) followed by calcination and (i) fluoriding to not above 8% bulk F level, using a F-contg. soln. with pH 3.5-4.5 (pref. an aq. soln. of  $NH_4F/HF$ ), and heating from room temp. to 350-450 deg. C in air, an atmos. contg.  $O_2$ , or an inert gas within 3 h, or (ii) fluoriding to not above 10% bulk F content, using a fluoride soln. with pH less than 3.5 and heating at 350-450 (375-400) deg. C, in air, an atmos. contg.  $O_2$ ,  $H_2$  or an inert gas. The final calcination is for 1-5 h, and the catalyst is esp. activated in  $H_2$  at 350-450 deg. C for at least 1-48 hr.

**EXAMPLE**

(A) A 1/16 inch  $\text{Al}_2\text{O}_3$  extrudate carrying 0.3 wt. % Pt and 1% Cl was fluoridised in a soln. of  $\text{NH}_4\text{F}$  (pH 7.5), to deposit (I) 0.75% F or (II) 3% F, followed by standing at room temp. for 1 h, drying at 120 deg. C for 1 h, and calcining at 150 deg. C for 1 h, rising to 400 deg. C at 50 deg. C/15 mins and holding at 400 deg. C for 2 h.

The catalysts were heated from room temp. to 100 deg. C in  $\text{H}_2$  at 50 psi, 3 cubic ft/h during 2 h, at 100 deg. C for 1 h, to 350 deg. C during 2 h, at 350 deg. C for 1 h, followed by cooling to 300 deg. C. The N/Al ratio was: (I) -, (II) 0.0009.

(B) The catalysts were used to isomerise 600N slack wax with 22% oil, at 1000 psi  $\text{H}_2$  pressure,  $\text{H}_2$  gas rate 5000 SCF/B LHSV 0.9 vols./vol./h, and (I) 331, or (II) 296 deg. C. The max. 370+ deg. C dewaxed oil, wt. % w.r.t. feed, was: (I) 49.5, (II) 42.5; 370- deg. C, wt. % w.r.t. feed, was: (I) 34.4; (II) 28.5; catalyst activity, 40 h, was: (I) 1.0, (II) 19.0. (23pp510CGDwgNo0/6).

(E) ISR: No Search Report.