

85-124417/21 HO4 J04 SHEL 14.10.83  
 SHELL INT RES MIJ BV \*FR 2553-430-A  
 14.10.83-FR-016372 (19.04.85) B01j-21/08 B01j-23/56 C10g-73/44  
 C10m-101/02

Hydroisomerisation of petroleum wax high-activity catalyst - including refractory oxide support treated with a metal of gps. 2a, 3a, 4a or 4b

C85-053934 Hydroisomerisation process for petroleum waxes comprises contacting them with H<sub>2</sub> under hydroisomerization conditions in presence of a catalyst comprising: (i) hydrogenating metal or an oxide thereof, on (ii) refractory oxide which has been treated with (iii) 0.1-30 wt. % or cpd(s) of reacting metals or Periodic Gps. IIa, IIIa, IVa and/or IVb.

#### USE/ADVANTAGE

The process is useful for treating non-deoiled paraffins obtd. as by-prod. during prodn. of lubricating oils, esp. by hydrocracking. The hydroisomerised prod. can be used as lubricating oil fraction(s). Prods. of high or extremely high VI are obtd. in good selectivity without the usual loss of conversion and at moderate temps.: e.g. there is 70% conversion of a non-deoiled wax at 342 deg. C, with 59% selectivity to an oil yielding on fractionation lubricating oils of VI 154-156.

H(4-E, 4-E8) J(4-E1).

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#### PREFERRED CATALYST

Component (ii) is pref. Al<sub>2</sub>O<sub>3</sub>, MgO, ZrO<sub>2</sub>, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> or esp. SiO<sub>2</sub>, or their combinations. SiO<sub>2</sub> is pref. used in an essentially non-crystalline form of pore vol. 0.5 cc/g and specific surface 100-600 sq. m/g; the particles pref. have smallest dimension 0.1-30 nm, and more pref. are spherical, with dia. 0.5-10 nm.

Component (iii) is pref. a cpd. of Mg, Al, Ti and/or Zr, and its concn. (as oxide) is pref. 0.1-10 (esp. 1-7) wt. % of (ii). Al is pref., and can be applied by impregnating (ii) with a soln. of tetramethylammonium aluminate. Zr or Mg can be applied by impregnating (ii) with a soln. of the metal nitrate followed by a soln. of a hydrocarbyl ammonium hydroxide, the wt. ratio of refractory oxide to hydrocarbyl ammonium hydroxide being 1-100 (pref. 2-10). Ti can be applied as the soln. of an alcoholate, esp. Ti ethylate.

The impregnated refractory oxide may be dried at 50-250 deg. C and/or calcined in air at 250-1000 deg. C. If impregnation is by a 2-step method, there may be an intermediate calcination. Component (i) pref. comprises 0.1-2 wt. % of Gp. VIII noble metal, esp. Pt.

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**PROCESS CONDITIONS**

Hydroisomerization is pref. effected at 250-450 deg. C, 2-25 MPa pressure, space velocity 0.1-5 kg/1 catalyst x h, and with a feed ratio of 100-2500 Ni H<sub>2</sub>/kg feed. (17pp1492RKMHDwgNo0/0)

85-124361/21 H04 J04 L02 SHEL 14.10.83  
 SHELL INT RES MIJ BV \*FR 2553-302-A  
 14.10.83-FR-016373 (19.04.85) B01j-31/34 C10g-45/60  
 Refractory oxide useful as hydrogenation catalyst support - modified  
 by impregnating with soln(s) contg. alkyl ammonium ions and active  
 metal

H(4-F2E) J(4-E3, 4-E4B) L(2-G) N(1-B, 1-C, 1-D, 3-B, 3-G)

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C85-053916 Prod'n. method comprises impregnating  
 refractory oxide(s) with hydrocarbyl ammonium metallate(s)  
 and/or a mixt. contg. a hydrocarbyl ammonium ion and a  
 reactive metal from Periodic Gps. IIa, IIIa, IVa or IVb.

#### USE/ADVANTAGE

The modified oxides are useful as catalyst and catalyst  
 supports in hydrocarbon conversions, pref. in presence of  
 $H_2$ , esp. in hydrodearomatization of kerosenes and in hydro-  
 isomerization of petroleum waxes (FR 2,553,430). Catalyst  
 activity is improved, supposedly as a result of increased  
 acidity.

#### PREFERRED MATERIALS

The refractory oxide is pref.  $Al_2O_3$ , MgO,  $ZrO_2$ ,  $TiO_2$ ,  
 $Cr_2O_3$ ,  $B_2O_3$  or esp.  $SiO_2$  or their mixts., and is pref. non-  
 crystalline.  $SiO_2$  is pref. used in a form of pore vol. at  
 least 0.5 cc/g and surface area 100-600 sq. cm/g. and contg.

less than 12 wt. % water. The oxide particles pref. have a  
 smallest dimension of 0.1-30  $\mu$ m: esp. they are spheres of  
 dia. 0.5-10  $\mu$ m. The impregnating reactive metal(s) is pref.  
 Mg, Al, Ti or Zr. If the refractory oxide is  $SiO_2$ , the  
 impregnating metal is pref. Al.

#### PREPARATION

The hydrocarbyl ammonium cpds. used in impregnating  
 are pref. 1-4C alkyl, esp. tetramethyl-ammonium cpds. Al  
 can be added by impregnating with a soln. of tetramethyl-  
 ammonium aluminate. Zr and Mg (and Al) can be added as  
 solns. contg. the metal nitrates, followed by a soln. of the  
 hydrocarbyl ammonium hydroxide, pref. with wt. ratio of  
 the latter hydroxide to refractory oxide of 0.01-1 (esp. 0.1-  
 0.5). Ti, e.g., can be added as an alcoholate, esp. as a  
 soln. of  $Ti(OEt)_4$ . Impregnation may be by the wet method  
 or to dryness: with aq. solns., the temp. is pref. 60-90 deg.  
 C. After impregnation, the oxide is pref. dried at 50-250  
 deg. C and/or calcined in air at 250-1000 deg. C: in 2-step  
 impregnation, there may be calcination for 1-24 hr. at 250-400  
 deg. C after the first step, and for 1-24 hr at 400-800 deg.  
 C after the second.

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**CATALYST COMPOSITIONS**

The concn. of reactive metals in the refractory oxides is pref. 0.1-10 wt. %. The catalyst may also contain 0.1-2 wt. % Gp. VIII metal(s).

**EXAMPLE**

100 g dried  $\text{SiO}_2$  spheres (pore vol. 0.74 cc/g, specific surface 294 sq. m/g) were impregnated for 2 hr. at 70 deg. C followed by 16 hr at ambient temp., with an aq. soln. of tetramethylammonium aluminate obtd. by mixing an aq. soln. of 24 g  $\text{AlCl}_3$  with 388 cc  $\text{NMe}_4\text{OH}$  (10 vol. %) under  $\text{N}_2$ . The spheres were then dried at 100 deg. C for 1 hr. and at 200 deg. C for 3 hr. and finally calcined at 600 deg. C for 3 hr. The prod. contained 5.1 wt. %  $\text{Al}_2\text{O}_3$ , and had pore vol. 0.95 cc/g, and specific surface 346 sq. m/g. (17pp1492RKMHDwgNo0/0)