

CATALYST CONTAINING PHOSPHOROUS AND A PROCESS FOR HYDROTREATMENT OF PETROLEUM FEEDS USING THE CATALYST

The present invention concerns a catalyst for hydrotreatment of a hydrocarbon petroleum feed, comprising cobalt, molybdenum and phosphorous.

5 Hydrotreatment of petroleum cuts is gaining importance in refining, both with the increasing necessity for converting ever heavier fractions and with the increasing severity of specifications for the finished products.

This state of affairs arises from the economic importance of maximally upgrading imported crudes with ever-increasing heavy fractions which have both a relative deficit of hydrogen in those
10 heavy fractions or lighter fractions produced from them, and contain a large quantity of heteroatoms such as sulphur and nitrogen.

In general, hydrotreatment is the purification of hydrocarbon petroleum cuts without significant modification of the backbone defined by the carbon atoms. Thus it includes eliminating heteroatoms such as sulphur and nitrogen, eliminating metals, and partial or complete
15 hydrogenation. When this proves to be necessary, the petroleum cut is hydrotreated then freed of the products formed which means that a purified petroleum cut can be recovered.

The "severity" of hydrotreatment is directly linked to the operating conditions. The term "operating conditions" means the nature of the feed, the total pressure in the reaction zone, the partial pressures of the various compounds, the reaction temperature, the hourly space velocity and
20 the hydrogen flow rate. In general, the heavier the feed and/or more difficult it is to convert, the more severe are the operating conditions, i.e., the pressures, temperature and hydrogen flow rate are higher and the hourly space velocity is lower.

Our research on a variety of supports with a variety of compositions has led us to the discovery that, surprisingly, an alumina based catalyst containing, expressed as the oxide content by
25 weight, 2-10% by weight of cobalt oxide CoO, 10-30% by weight of molybdenum oxide MoO₃ and

4-10% of phosphorous oxide P_2O_5 and which preferably has particular physico-chemical characteristics, has a hydrotreatment activity which is far superior to those of prior art formulations.

The matrix used is alumina based (at least 50% by weight of alumina) and is preferably essentially constituted by alumina.

5 The catalyst is characterized in that the phosphorous content, expressed as the percentage by weight of phosphorous pentoxide P_2O_5 , with respect to the finished catalyst, is in the range 4.0% to 10.0%, preferably in the range 4.5% to 8.0% and more preferably in the range 5.6% to 8.0% or 5.6% to 6.5%. It is characterized in that the cobalt content, expressed as the percentage by weight of cobalt oxide CoO with respect to the finished catalyst, is in the range 2.0% to 10.0%, preferably in
10 the range 3.5% to 7.0% and more preferably in the range 3.5% to 5.5%. It is characterized in that the molybdenum content, expressed as the percentage by weight of molybdenum oxide MoO_3 with respect to the finished catalyst, is in the range 10% to 30%, advantageously in the range 10% to 18.9%, preferably in the range 15.0% to 18.9% and more preferably in the range 16.0% to 18.5%.

The catalyst is also characterized by:

15 BET surface area: The BET surface area, measured on the finished catalyst, is in the range 100 to 300 m^2/g , preferably in the range 120 to 250 m^2/g and more preferably in the range 130 to 240 m^2/g .
CSH: the Shell crushing strength, termed CSH, measured on the finished catalyst, is more than 1.4 MPa and preferably more than 1.6 MPa.

Average pore diameter: The average pore diameter is measured from the pore distribution profile
20 obtained using a mercury porosimeter. From the pore distribution curve, the derivative curve can be calculated. This derivative curve passes through one or more maxima, the abscissa of which gives the pore diameter. The catalyst claimed is such that the maximum or maxima is/are obtained for a pore diameter or diameters in the range 80 Å to 110 Å (10 Å = 1 nm), preferably in the range 95 Å to 110 Å, more preferably in the range 100 Å to 110 Å.

Pore volume of pores below 80 Å: The pore volume of pores with a diameter of less than 80 Å is at most 0.05 ml/g, preferably at most 0.035 ml/g and more preferably at most 0.025 ml/g.

Pre volume of pores over 140 Å: The pore volume of pores with a diameter of over 140 Å is less than 0.08 ml/g, preferably less than 0.06 ml/g and more preferably less than 0.05 ml/g. There are practically no pores of over 250 Å, more generally their pore volume is less than 10% of the total pore volume, or more preferably less than 8%.

Pore volume of pores in the range 80 Å to 140 Å: The pore volume of pores with a diameter in the range 80 Å to 140 Å is in the range 0.20 ml/g to 0.80 ml/g, preferably in the range 0.30 ml/g to 0.70 ml/g and 20-60% of the total pore volume is in pores with a diameter 100-130 Å.

The catalyst of the present invention can be prepared using any one of the methods which are known to the skilled person.

The hydrogenating element is introduced during mixing or after forming (as is preferred).

Forming is followed by calcining, the hydrogenating element being introduced before or after calcining. Preparation is finished in all cases by calcining at a temperature of 250°C to 600°C.

One preferred method consists of mixing a moist alumina gel for several tens of minutes then passing the paste obtained through a die to form extrudates with a diameter which is preferably in the range 0.4 to 4 mm.

The catalyst also comprises a hydrogenating function. The hydro-dehydrogenating function is provided by molybdenum or cobalt. It can be introduced into the catalyst at various stages in the preparation and in various ways.

It may be introduced partially or completely on mixing with the gel of the oxide selected as the matrix, the remaining hydrogenating element(s) being introduced after mixing, more generally after calcining.

Molybdenum is preferably introduced simultaneously with or after the cobalt, whatever the method of introduction.

It is preferably introduced by one or more ion exchange operations carried out on the calcined support using solutions containing the precursor salts of the metals.

It can be introduced by one or more operations for impregnating the formed and calcined support with a solution of one or more precursors of cobalt oxide while the molybdenum oxide precursor(s) is/are introduced prior to that during mixing of the support.

When the elements are introduced in several steps for impregnating the corresponding precursor salts, an intermediate calcining step must be carried out on the catalyst at a temperature which is in the range 250°C to 600°C.

Phosphorous is introduced at any stage of the preparation. It can be introduced alone or mixed with cobalt and/or molybdenum. It can, for example, be introduced before peptising the alumina. It can also, for example, be introduced into the alumina extrudate with or without intermediate calcining. It can also be completely or partially introduced, mixed with the cobalt or the molybdenum, into the alumina which is in the form of an extrudate, with or without intermediate calcining. It can also be completely or partially introduced with the cobalt and molybdenum, into the alumina which is in the form of an extrudate, with or without intermediate calcining. It can also be introduced lastly and alone. Finally, it should be noted that this list is given by way of indication only and a large number of variations can be imagined.

Since these metallic elements are introduced in the form of oxides, in order to become active they have to be sulphurised. It should be noted that any in-situ or ex-situ sulphurisation method is suitable.

The invention also concerns a hydrotreatment process using this catalyst.

Many different feeds can be treated from naphtha (initial boiling point 80°C) to vacuum distillates or vacuum residues.

The total pressure is in the range 0.5 to 20 MPa, the temperature is in the range 200°C to 480°C, preferably in the range 260°C to 450°C, the hourly space velocity is in the range 20 to 0.05

h^{-1} and the hydrogen flow rate is in the range 100 to 3000 litres per litre of feed. The hydrogen partial pressure is preferably relatively low, at 0.5-6 MPa, preferably 0.5-5 MPa. To take two extremes as examples, hydrodesulphuration of a naphtha cut was carried out at a pressure of 1.5 MPa, a temperature of 300°C , an hourly space velocity of 10 h^{-1} and a hydrogen flow rate of 100 l/l of feed while hydrodesulphuration of a deasphalted vacuum residue was carried out at a pressure of 20 MPa, a temperature of 390°C , an hourly space velocity of 0.5 h^{-1} and a hydrogen flow rate of 1500 l/l of feed.

The following examples illustrate the present invention without in any way limiting its scope.

We produced a large quantity of an alumina based support. To this end, we used a commercially available SB3 gel sold by Condea. The gel was mixed with water and nitric acid then mixed for 15 minutes. Following mixing, the paste obtained was passed through a cylindrical die to obtain extrudates with a diameter of 1.2 mm. The extrudates were then dried overnight at 120°C then calcined at 550°C for 2 hours in moist air containing 7.5% by volume of water.

EXAMPLE 1: Catalyst C1, not in accordance with the invention

Cobalt, molybdenum and phosphorous were added to the extruded support. The salts of these three elements were introduced simultaneously by dry impregnation of the support. The cobalt salt used was cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The molybdenum salt was ammonium heptamolybdate $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ and the phosphorous was introduced in the form of H_3PO_4 . After dry impregnation, the extrudates were dried overnight at 120°C then calcined at 550°C for 2 hours in moist air containing 7.5% by volume of water. The final quantities of metal oxides and the principal physico-chemical characteristics were thus as follows:

MoO_3 (% by weight)	:	18.2
CoO (% by weight)	:	4.1
P_2O_5 (% by weight)	:	1.9
S_{BET} (m^2/g)	:	205
CSH (MPa)	:	1.3

EXAMPLE 2: Catalyst C2, in accordance with the invention

Cobalt, molybdenum and phosphorous were added to the extruded support. The salts of these three elements were introduced simultaneously by dry impregnation of the support. The cobalt salt used was cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The molybdenum salt was ammonium heptamolybdate $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ and the phosphorous was introduced in the form of H_3PO_4 . After dry impregnation, the extrudates were dried overnight at 120°C then calcined at 550°C for 2 hours in moist air containing 7.5% by volume of water. The final quantities of metal oxides and the principal physico-chemical characteristics were thus as follows:

MoO ₃ (% by weight)	:	18.2
CoO (% by weight)	:	4.1
P ₂ O ₅ (% by weight)	:	5.7
S _{BET} (m ² /g)	:	170
CSH (MPa)	:	1.8

EXAMPLE 1: Catalyst C3, not in accordance with the invention, for reference

Cobalt and molybdenum were added to the extruded support. The salts of these elements were introduced simultaneously by dry impregnation of the support. The cobalt salt used was cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and the molybdenum salt was ammonium heptamolybdate $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$. After dry impregnation, the extrudates were dried overnight at 120°C then calcined at 550°C for 2 hours in moist air containing 7.5% by volume of water. The final quantities of metal oxides and the principal physico-chemical characteristics were thus as follows:

MoO ₃ (% by weight)	:	18.2
CoO (% by weight)	:	4.1
P ₂ O ₅ (% by weight)	:	0
S _{BET} (m ² /g)	:	235
CSH (MPa)	:	1.2

EXAMPLE 4: Comparative test: Hydrogenation of toluene

The activity of the three catalysts described above were compared by hydrogenation of toluene. Before use, the catalysts were sulphurised in situ. The reaction was carried out at 3 MPa at

a temperature of 300°C. The feed was constituted by toluene to which 2% by weight of DMDS had been added. the relative activities are shown in the table below. Catalyst C3, which contained no phosphorous, was selected as the reference.

Catalyst	Activity
C1	126
C2	152
C3	100

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It can be seen that the two catalysts containing phosphorous were more active than the catalyst with no phosphorous. Further, it can be seen that the catalyst which contained a high proportion of phosphorous was significantly more active than that containing only a little.

EXAMPLE 5: Comparative test: HDS of SRGO

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The three catalysts described above were compared using an actual feed. Before use, the catalysts were sulphurised in-situ. We measured the hydrodesulphurising activity on a straight run gas oil, the principal characteristics of which are given in the table below:

Density at 15°C	0.856
Refractive index at 20°C	1.4564
Viscosity at 50°C	3.72 cSt = $3.72 \times 10^{-6} \text{ m}^2/\text{s}$
Sulphur	1.57% by weight
Simulated distillation:	
IP	153°C
5%	222°C
50%	315°C
95%	415°C
EP	448°C

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The HDS test on the gas oil was carried out under the following operating conditions:

Total pressure	3 MPa
Hourly space velocity	2 h ⁻¹
Temperature	310°C, 340°C and 360°C
Hydrogen flow rate	250 l/l of feed

The catalytic performances of the three catalysts at the three reaction temperatures are given in the following table. They are expressed as the activity using the activity at each temperature of catalyst C3, which did not contain phosphorous, as the reference.

Catalyst	310°C	340°C	360°C
C1	117	115	118
C2	123	128	129
C3	100	100	100

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Catalyst C2 of the invention was apparently be significantly more active.

The catalyst of the invention is thus particularly suitable for hydrodesulphuration.

CLAIMS

1. An alumina based catalyst containing, expressed as the oxide content by weight, 2-10% by weight of cobalt oxide CoO , 10-30% by weight of molybdenum oxide MoO_3 and 4-10% of phosphorous oxide P_2O_5 , with a BET surface area in the range 100-300 m^2/g , a crushing strength CSH of more than 1.4 MPa, and an average pore diameter in the range 8-11 nm, the pore volume of pores with a diameter of more than 14 nm being less than 0.08 ml/g, the volume of pores with a diameter of less than 8 nm being at most 0.05 ml/g, and the volume of pores with a diameter which is in the range 8 to 14 nm being in the range 0.20 ml/g to 0.8 ml/g.
2. A catalyst according to any the preceding claim, in which the P_2O_5 content is 4.5-8.0%.
3. A catalyst according to any one of the preceding claims, in which the P_2O_5 content is 5.6-8.0%.
4. A catalyst according to any one of the preceding claims, in which the CoO content is 3.5-7.0% and the MoO_3 content is 10.0-18.9%.
5. A catalyst according to any one of the preceding claims, prepared by impregnating a calcined alumina based matrix with solution(s) of cobalt, molybdenum and phosphoric acid, followed by drying and calcining in moist air.
6. A process for hydrotreatment of petroleum feeds using a catalyst according to any one of claims 1 to 5, operating at a temperature of 200-480°C, at a pressure of 0.5-20 MPa, with an hourly space velocity of 0.05-20 h^{-1} and a hydrogen flow rate of 100-3000 l/l of feed.
7. A process according to claim 6, carried out between 0.5 and 6 MPa.
8. A process according to claim 6 or claim 7, in which the hydrotreatment is hydrodesulphuration.

