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(54) Title: PROCESS FOR SELECTIVELY SULFIDING A SUPPORTED NICKEL CATALYST

(57) Abstract: The present invention relates to a process for selectively sulfiding a supported nickel catalyst, a supported nickel catalyst sulfided by the present process and uses of said catalyst.



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PROCESS FOR SELECTIVELY SULFIDING A SUPPORTED NICKEL
CATALYST

The present invention relates to a process for selectively sulfiding a supported nickel catalyst, a supported nickel catalyst sulfided according to said process and a process for hydrotreating, in particular for the hydrogenation, of a hydrocarbon feed using said catalyst.

The sulfidation of nickel containing catalysts has been sufficiently described. The known processes can be essentially classified into ex situ and in situ processes.

According to the in situ processes the catalysts are treated in the reactor with a sulfur (S)-containing compound (H_2S , COS , CS_2 , mercaptan, polysulfide or other organic compounds) in the presence of hydrogen just prior to catalytic reaction.

US 6,059,956, US 4,530,917 and EP 0 352 851 disclose ex situ processes. According to US 6,059,956 the catalysts to be sulfided are loaded with a sulfur containing compound (e.g. organic polysulfides, mercaptans, disulfide) followed by treatment with hydrogen at temperatures of 150-700 °C, and are stabilised at ambient temperature after cooling in a stream of inert gas.

US 4,530,917 discloses an in situ impregnation of the catalyst with an organic solvent in which a polysulfide is dissolved. The impregnated catalyst is integrated in a technical reactor and is subjected to an in situ hydrogen treatment. Thereby metal sulfides are formed. EP 0 352 851 discloses the impregnation of

catalysts with aqueous solutions of S-containing compounds followed by hydrogen treatment.

GB1009590A discloses a hydrogenation catalyst made by treating finely divided or dispersed elementary nickel with a free oxygen-containing gas, whereby the nickel surface is oxidized, the catalyst intermediary so obtained being treated with (a) elementary sulfur or (b) an organic sulfur compound or (c) H₂S or (d) CS₂ or (e) a mixture of two or more of (a), (b), (c) and (d), the treatment being effected such that a minor proportion of the nickel present in the catalyst is brought into association with sulfur. Certain sulfur-containing compounds are described in GB1009590A as effecting only a limited degree of deactivation. Elemental sulfur and other sulfur-containing compounds such as H₂S and CS₂, on the other hand, are not placed in this category, and are taught to lead to progressive sulfidation, which eventually leads to bulk sulfidation of the catalyst.

Various of the sulfidation processes known so far prove especially useful for sulfidations wherein a bulk sulfidation is desired. However, if only part of the metal is intended to become sulfided as is required for the hydrogenation of diolefins into monoolefins, the known processes result in uneven thicknesses of layers of metal sulfide phases and thus an inhomogenous distribution of the active components associated with an unsatisfying performance of the hydrotreating catalysts.

The technical problem underlying the present invention is therefore to provide processes for selectively sulfiding catalysts and catalysts obtained thereby which overcome the above-identified disadvantages. In particular the technical problem underlying the present invention is to provide processes

for selectively sulfiding supported catalysts which processes provide highly active and selectively sulfided catalysts, preferably for use in the hydrogenation of unsaturated hydrocarbons, in particular diolefins.

5 The present invention solves its problems by the provision of a process for selectively sulfiding a supported nickel (Ni) catalyst, which process comprises, preferably in said order, a) providing a reduced, and preferably passivated, supported nickel catalyst
10 containing in the range of from about 8 to about 20 weight% nickel (calculated as NiO on total catalyst weight) with a reduction level in the range of from about 30 to about 70% and b) sulfiding said supported catalyst with a mixture of an inert gas and H₂S at a temperature
15 below about 100°C so as to obtain a selectively sulfided supported nickel catalyst.

 The present invention solves the problem also by the provision of a sulfided, in particular selectively sulfided, supported nickel catalyst prepared according to
20 the process of the present invention.

 The present invention solves the problem also by the provision of a process for hydrotreating a hydrocarbon feed, in particular for selectively hydrotreating a hydrocarbon feed, wherein the feed is contacted with the
25 catalyst according to the present invention.

 Despite the teaching of the prior art that H₂S is a bulk sulfidation agent, according to the process of the present invention, by sulfiding a partly reduced catalyst with a mixture of an inert gas and H₂S at a temperature
30 below about 100°C, sulfided Ni-supported catalysts are obtained which exhibit a very high activity and stability, preferably in the hydrogenation of unsaturated hydrocarbons, particularly of diolefins and styrene.

According to the present process the sulfidation with H_2S takes place on the partly reduced and preferably passivated catalyst at a relatively low temperature below about $100^\circ C$ and in the presence of inert gas.

5 Without wishing to be bound by theory, obviously, a bulk sulfidation is avoided in the process of the present invention by preferential sulfidation of the Ni-O-phase in the catalyst and a homogenous distribution of sulfur across the catalyst is surprisingly and advantageously
10 achieved thereby.

According to the invention, a distribution of non-crystalline Ni-O-phases in the catalyst provided in step a) can be made use of, under step b), by preferentially sulfiding the Ni-O phase, to achieve selective
15 sulfidation, which avoids uneven thicknesses of layers of metal sulfide phases and thus an inhomogenous distribution of the active components in resulting catalysts.

Therefore, the sulfiding in step b) may optionally
20 be described as being preferential towards the Ni-O phase of the catalyst, compared to crystalline NiO of the catalyst. Such preferential sulfiding may preferably be carried out under conditions that are more effective for sulfiding one or more amorphous Ni-O phases than for
25 sulfiding crystalline NiO. Relative sulfiding effectiveness may conveniently be determined by a comparison of sulfiding reaction rates.

Optionally, the sulfiding in step b) may be preferential so as to cause the sulfidation level by
30 weight of at least one Ni-O phase in the catalyst to be at least 50%, preferably at least 200%, and ideally at least 400% higher than the sulfidation level by weight of crystalline NiO in the catalyst.

In the context of the catalysts obtained by the present invention, the term "selectively" means only partially sulfided nickel, preferably to sulfide in the range of from about 8 to about 16% by weight of the nickel present in the total catalyst composition provided in step a). Additionally or alternatively the sulfided catalysts of the invention may comprise in the range of from about 0.5% to about 5%, preferably from about 0.6% to about 3%, and most preferably from about 0.7% to about 2% by weight of sulfur.

Weight-% values given in the present teaching refer, if not otherwise said, to the weight of the dry total catalyst. In the context of the present invention, the components of the catalyst are to be selected in an overall amount to add up to 100 weight%, in particular do not exceed 100 weight%.

In a preferred embodiment of the present invention a process for selectively sulfiding a supported nickel catalyst consisting of steps a) and b) is provided, thereby excluding any other process steps so as to obtain a sulfided supported nickel catalyst according to the present invention.

In a further preferred embodiment, the selectively sulfided catalyst obtained in step b) is subsequently passivated (hereinafter also called stabilised).

In a preferred embodiment of the present invention the reduced and passivated catalyst provided in step a) may be sulfided in step b), and optionally subsequently passivated, in one and the same reactor. In a furthermore preferred embodiment the reduced and passivated catalyst provided in step a) may have been reduced and passivated in a separate facility and therefore the sulfiding in step b), and optionally the subsequent passivation, may

preferably take place in a separate sulfidation reactor, for instance in a fluidized catalyst bed. In a furthermore preferred embodiment the sulfiding in step b) of the reduced and passivated catalyst provided according to step a) is carried out in the hydrotreating, preferably hydrogenation reactor itself.

The process according to the invention can thus be carried out ex situ or in situ. In the context of the present specification, the term in situ means in the reactor in which the catalyst will eventually be applied to effect hydrotreating. Conversely, ex situ means outside said reactor. It is preferred to carry out the process according to the invention ex situ, because this generates less downtime for the hydrotreating reactor and simplifies the reactor start-up.

If the process according to the invention is carried out ex situ, it may be desirable to passivate the sulfided catalyst prepared in this way, since sulfided catalysts may be self-heating. Passivation can be done by contacting the sulfided catalyst with an oxygen-containing compound under controlled conditions. The use of an oxygen-containing gas, such as air, is a well-known embodiment. Alternatively, the sulfided catalyst may be passivated by being contacted with an organic liquid, such as diesel, gas oil, white spirit, or lube oil. Passivation processes are known in the art.

The total pressure during the process according to the invention is not critical. It will generally be between atmospheric pressure and about 300 bar, depending on where the process is carried out. If the process is carried out ex situ, the pressure may, e.g., be between atmospheric pressure and about 10 bar. If the process is

carried out in situ, the pressure may be much higher, e.g., in the range of about 25 to about 300 bar.

A relatively low temperature below about 100°C during step b) is important according to the invention for avoiding bulk sulfidation and enabling selective sulfidation. Advantageously, the temperature during step b) may be at least 20°C, or greater than 20°C. In particularly preferred embodiments of the present invention, to provide conditions particularly suitable for selective sulfidation, the sulfiding in step b) is carried out at a temperature in the range of from about 25 to about 90 °C, more preferably in the range of from about 40 to about 70 °C. The temperature will of course generally fluctuate within the above ranges during sulfiding, particularly given the exothermic nature of the process.

Other conditions that may support selective sulfidation in accordance with the present invention are: H₂S content in the gas mixture used in step b); gas loading in step b); and exposure time in step b). These conditions can be adjusted to provide particularly effective and convenient selective sulfidation in accordance with the invention.

Thus, in a preferred embodiment of the present invention the mixture of the inert gas, which is preferably nitrogen, and H₂S (hydrogen sulfide) has a H₂S content in the range of from about 250 to about 10 000 vppm (volumes part per million), preferably in the range of from about 1 500 to about 3 500 vppm.

In a furthermore preferred embodiment of the present invention the sulfiding in step b) is carried out with a gas load in the range of from about 1 000 to about 6 000 v/vh (volume gas per volume catalyst and hour, m³/m³h),

preferably in the range of from about 2 500 to about 4 000 v/vh.

In a furthermore preferred embodiment of the present invention, the exposure time for the sulfiding in step b) is in the range of from about 1 to about 3 hours.

Whilst the preferred conditions recited above may be deployed alone or in any combination, in a particularly preferred embodiment of the present invention, the H₂S content in the gas mixture, the gas loading level and the exposure time during step b) may all be within the ranges recited above to ensure preferential sulfidation in accordance with the invention that leads to selectively sulfided catalysts which are especially active and selective.

In a furthermore preferred embodiment of the present invention the sulfided supported nickel catalyst obtained in step b) is subsequently stabilised, preferably in an oxygen/nitrogen mixture or an air/nitrogen mixture.

In a furthermore preferred embodiment of the present invention the sulfiding in step b) is carried out in a moving bed, also called fluidized bed. Such an embodiment avoids local overheating, which is particularly advantageous in the context of the temperature range essential in the present invention.

In a furthermore preferred embodiment of the present invention the sulfiding in step b) is carried out in a fixed bed.

The presence of an inert gas in the mixture used in step b) supports and maintains selective sulfidation. The sulfiding in step b) may thus advantageously be carried out in an inert environment, i.e. in essentially non-reductive conditions, or in conditions which do not cause

any (substantial and/or measurable) increase of the reduction level of the catalyst provided under step a).

A substantial increase in the reduction level would have the effect of reducing the activity and/or selectivity of the sulfided catalysts measurably, presumably by the mechanism of making further Ni-O phases available for sulfiding. Ultimately, the presence of a reducing agent such as hydrogen could even lead to bulk sulfidation, i.e. total loss of selectivity.

To maintain a high level of selectivity, the process of the invention may advantageously comprise an inerting step to reduce, mitigate or eliminate the presence of hydrogen and/or other reducing agents before, during and/or after the sulfiding in step b).

For example, in a furthermore preferred embodiment of the present invention, the invention foresees that prior to sulfiding the catalyst in step b) the reduced and passivated supported nickel catalyst is inertised.

In a furthermore preferred embodiment of the present invention, the sulfided supported nickel catalyst obtained in step b) is inertised, preferably prior to stabilising the catalyst.

In a furthermore preferred embodiment of the present invention the reduced and passivated supported nickel catalyst is inertised prior to the sulfiding in step b) and is furthermore inertised subsequent to the sulfiding in step b).

In a preferred embodiment of the present invention, the inerting is achieved by contacting the catalyst with a nitrogen stream. Advantageously, the catalyst provided in step a) may be contacted with an inert gas stream, or maintained in an inert gas atmosphere, before and/or during the sulfiding of step b), save for the

introduction or addition of H_2S into the inert gas stream during sulfiding in step b). Conveniently, the inert gas stream or atmosphere may comprise nitrogen.

5 In a preferred embodiment of the present invention the catalyst comprises, in particular essentially consists, and most preferred, consists of nickel and a support, hereinafter also called carrier. In a preferred embodiment of the present invention, the amount of nickel and of the support of the catalyst provided by step a)
10 add up to 100 weight% (total dry weight).

The catalyst carrier may comprise the conventional oxides, e.g., alumina (Al_2O_3), silica (SiO_2), silica-alumina, alumina with silica-alumina dispersed therein, silica-coated alumina, magnesia, zirconia, boria, and
15 titania, as well as mixtures of these oxides. As a rule, preference is given to the carrier comprising alumina, silica-alumina, alumina with silica-alumina dispersed therein, or silica-coated alumina. Special preference is given to the carrier consisting essentially of alumina or
20 alumina containing up to 25 wt.% of other components, preferably silica. A carrier comprising a transition alumina, for example an eta, theta, or gamma alumina is preferred within this group, with a gamma-alumina carrier being especially preferred. Additionally, the catalyst
25 may contain 0-60 wt.% of a zeolite.

The catalyst is preferably a shaped or moulded catalyst, preferably in the form of spheres, balls, tablets, pellets, beads, or extrudates. Highly suitable
30 are cylindrical particles, which may be hollow or not, as well as symmetrical and asymmetrical polylobed particles, preferably with 2, 3 or 4 lobes.

The catalyst may also be in form of a powder, in particular for use in suspension or slurry reactions.

The reduction level of the nickel in the catalyst provided in step a) of the present process is in the range of from about 30 to about 70%, expressed as the ratio of metallic nickel to total nickel, and may preferably be in the range of from about 40 to about 60%.

By virtue of its reduction level, the catalyst provided in step a) advantageously comprises a distribution of Ni-O-phase that can be made use of in the process of the invention for selective sulfidation, to provide a catalyst with a discontinuous but homogenous distribution of active components. The catalyst provided in step a) may be produced by conventional impregnation and reduction techniques.

In a preferred embodiment of the present invention the sulfided supported nickel catalyst obtained in step b) is a catalyst wherein in the range of from 8 to 16% by weight of the nickel is sulfided. Additionally or alternatively the sulfided catalysts of the invention may comprise in the range of from about 0.5% to about 5%, preferably from about 0.6% to about 3%, and most preferably from about 0.7% to about 2% by weight of sulfur.

In a further embodiment, the present invention relates to a process for hydrotreating a hydrocarbon feed, in particular for the selective hydrogenation of a hydrocarbon feed, by contacting the feed with the above catalyst at appropriate hydrotreating conditions.

The hydrotreating preferably takes place under conventional hydrotreating conditions, such as temperatures in the range of from about 70° to about 500 °C, preferably about 250 to about 450 °C., pressures in the range of from about 1 to about 250 bar, preferably about 5 to about 250 bar, and space velocities in the

range of from about 0,1 to about 10 h⁻¹. Examples of suitable feeds include middle distillates, kerosine, naphtha, vacuum gas oils, heavy gas oils and residues. Preferably, the hydrocarbon feed contains at least about 0.2 wt% of sulfur, calculated as atomic sulfur S. Examples of suitable hydrotreating reactions are hydrodesulfurisation, hydrocracking, hydrodenitrogenation, hydrodearomatisation, and hydrodemetallisation. Hydrodesulfurisation, hydrodenitrogenation, and hydrodearomatisation are preferred.

In a preferred embodiment of the present invention the hydrotreating is preferably a hydrogenation, in particular of diolefins and styrene containing feeds so as to obtain monoolefine and ethylbenzene containing products.

In a furthermore preferred embodiment of the present invention there is provided a process for hydrotreating, in particular for the hydrogenation of a hydrocarbon feed, preferably unsaturated hydrocarbons, in particular unsaturated aliphatic and aromatic hydrocarbons, in particular diolefines and styrene so as to prepare hydrogenated hydrocarbons, and preferably monoolefines and ethylbenzene.

Further preferred embodiments of the present invention are the subject matter of the subclaims.

The invention will be illustrated by way of example.

Example 1 (according to the invention)

200 ml of a passivated and reduced Ni-Al₂O₃ catalyst (Ni content 10.1 weight%, level of reduction: 41%) is inertised in a fixed bed reactor at ambient temperature for 1 h in a stream of nitrogen. Then the catalyst is treated for 2 h at the same temperature with 600 l/h of a

mixture of H₂S/N₂ comprising 10 000 vppm H₂S. Then the catalyst is inertised in nitrogen (60 l/h) followed by stabilisation for 2 h with a mixture of 1% by volume of O₂/N₂. The sulfided catalyst contains 1.06 weight% of S (sulfur).

Example 2 (according to the invention)

200 ml of a passivated and reduced Ni-Al₂O₃ catalyst (Ni content 10.1 weight%, level of reduction: 41%) is inertised in a fixed bed reactor at ambient temperature for 1 h in a stream of nitrogen and then heated to 70 °C. Then the catalyst is treated for 65 min at the same temperature with 600 l/h of a mixture of H₂S/N₂ comprising 2500 vppm H₂S and then cooled to room temperature in a stream of N₂ followed by stabilisation as described in example 1. The sulfided catalyst contains 1.26 weight% of S (sulfur).

Example 3 (comparative example)

16 ml of a commercial, passivated, reduced and SULFICAT®-sulfided (Eurecat) Ni-Al₂O₃ catalyst Ni content: 10.6 weight%, S content: 1.41 weight%) is heated to 120 °C in a stream of hydrogen (50 l/h) with a heating rate of 120 °C/h and treated with a hydrogen stream for 2 h at that temperature. Then the catalyst is heated to 200 °C with the same heating rate and kept for 2 h at that temperature in a stream of hydrogen. Then the reduced and sulfided catalyst is cooled down in a stream of hydrogen to the temperature of the hydrogenation. The sulfided catalyst contains 1.45 weight% of S (sulfur).

Comparison

The activity and selectivity of the sulfided catalysts obtained in Examples 1 to 3 was compared during hydrogenation using a synthetic feed of 3 % Isoprene / 1 % Indene / 75ppm S as Hexanthiol C₆H₁₂ balance. The

results shown in Table 1 below demonstrate the enhanced activity and selectivity of the catalysts according to the present invention.

Table 1

Catalyst	Ni-Content [%]	S-Content [%]	Relative Activity [%]	Relative Selectivity [%] ¹
Example 1 (according to the invention)	10.1	1.06	127	90
Example 2 (according to the invention)	10.1	1.26	121	91
Example 3 (comparative example)	10.6	1.45	100	88

Conditions of testing: GHSV = 2000 v/vh, LHSV = 4 v/vh, p = 40 bar

¹defined as conversion of Isoprene at 50 % Indene - conversion

C L A I M S

1. A process for selectively sulfiding a supported nickel catalyst, which comprises

a) providing a supported nickel catalyst containing in the range of from 8 to 20 weight% nickel with a reduction
5 level in the range of from 30 to 70% and

b) sulfiding said supported catalyst with a mixture of an inert gas and H₂S, at a temperature below 100°C, so as to obtain a selectively sulfided supported nickel catalyst.

10 2. The process according to claim 1, wherein the sulfiding in step b) is carried out with a gas load in the range of from 1 000 to 6 000 v/vh.

3. The process according to claim 1 or 2, wherein the mixture has a H₂S content in the range of from 250 to
15 10 000 vppm.

4. The process according to any one of claims 1 to 3 wherein the exposure time in step b) is in the range of from 1 to 3 hours.

5. The process according to any one of claims 1 to 4,
20 wherein the sulfiding in step b) is carried out at a temperature in the range of from 25 to 90 °C.

6. The process according to any one of claims 1 to 5 further comprising an inerting step to reduce, mitigate or eliminate the presence of hydrogen and/or other
25 reducing agents before and/or during the sulfiding in step b).

7. The process of any one of claims 1 to 6, wherein the catalyst provided in step a) is contacted with an inert gas stream before and/or during the sulfiding of step b),

save for the introduction of H₂S into the inert gas stream during sulfiding in step b).

8. The process according to any one of claims 1 to 7, wherein the sulfided catalyst obtained in step b) is stabilised.

9. The process according to any one of claims 1 to 8, wherein the sulfiding in step b) is carried out in a moving bed.

10. The process according to any one of claims 1 to 9, wherein the sulfided catalyst obtained in step b) is inertised.

11. The process according to any one of claims 1 to 10 wherein the sulfided catalyst obtained in step b) comprises in the range of from 0.5% to 5% by weight sulfur.

12. The process according to any one of claims 1 to 11, wherein the sulfiding in step b) is preferential towards an Ni-O phase in the catalyst, compared to crystalline NiO in the catalyst, so as to cause the sulfidation level by weight of at least one Ni-O phase in the catalyst to be at least 200% higher than the sulfidation level by weight of crystalline NiO in the catalyst.

13. A selectively sulfided supported nickel catalyst obtainable according to any one of the processes of claims 1 to 12.

14. A process for hydrotreating a hydrocarbon feed, wherein the feed is contacted with a catalyst according to claim 13 at hydrotreating conditions.

15. A process according to claim 14, wherein the feed is a diolefine or styrene feed.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J27/043 B01J37/20 C07C5/05 C10G45/36 C10G49/04
B01J23/755

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C07C C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 0 307 520 A (UOP INC [US]) 22 March 1989 (1989-03-22) claim 7; examples A-C; table 1 -----	13-14
X	GB 1 009 590 A (BRITISH PETROLEUM CO; PETER DESMOND HOLMES; KENNETH HUGH BOURNE) 10 November 1965 (1965-11-10) column 1, line 34 - column 1, lines 41-43; example 1; table 1 column 2, lines 70-74 ----- -/--	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	HOFFER B W ET AL: "Enhancing the start-up of pyrolysis gasoline hydrogenation reactors by applying tailored ex situ presulfided Ni/Al ₂ O ₃ catalysts" FUEL, IPC SCIENCE AND TECHNOLOGY PRESS, GUILDFORD, GB, vol. 83, no. 1, 1 January 2004 (2004-01-01), pages 1-8, XP004456108 ISSN: 0016-2361 example Experimental	1-15
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A	page 433, column 1, line 33 - column 2, line 36; table 1 page 433, column 2, lines 24-36	1-12
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A	page 29, column 1, lines 33-63; figure 5 page 29, column 1, lines 33-63	1-12
X	US 5 248 648 A (BREYSSE MICHELE [FR] ET AL) 28 September 1993 (1993-09-28) examples 1-3	13-14
A	examples 1,3	1-12

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