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(54) Title: PROCESS FOR SULFUR ADSORPTION USING COPPER-CONTAINING CATALYST

(57) **Abrégé/Abstract:**

The present invention is a method for the adsorption of sulfur-containing compounds from a hydrocarbon feedstream, and in particular, an olefin feedstream. The method comprises contacting the sulfur-containing compound with a copper oxide / zinc oxide / aluminum oxide catalyst optionally promoted with a metal.



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(54) Title: PROCESS FOR SULFUR ADSORPTION USING COPPER-CONTAINING CATALYST

(57) Abstract: The present invention is a method for the adsorption of sulfur-containing compounds from a hydrocarbon feedstream, and in particular, an olefin feedstream. The method comprises contacting the sulfur-containing compound with a copper oxide / zinc oxide / aluminum oxide catalyst optionally promoted with a metal.



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Title: Process for Sulfur Adsorption Using Copper-Containing Catalyst
Inventors: Turbeville et al

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Background of Invention

This invention is directed to catalysts and related processes useful for sulfur adsorption from sulfur compound containing feedstreams. Specifically, the invention is directed to copper oxide / zinc oxide / aluminum oxide catalyst optionally promoted with an alkali metal, such as K, Rb, Cs, or with a metal selected from the group consisting of Ti, V, Mn, Zr, Mo, Ru, Rh, Pd, Ba, La, Re, Tl, Ce and combinations thereof, useful for sulfur adsorption processes.

As used herein, the term adsorption shall be defined broadly so as to also include absorption, and no attempt shall be made to distinguish adsorption or adsorptive processes from absorption or absorptive processes.

As part of the pretreatment of naphtha feed streams for catalytic reformers and isomerization units, sulfur guards are commonly used to polish the remaining sulfur species that are present after a hydrotreater. Guard materials often contain either reduced nickel or copper oxide. Nickel adsorbents are very effective at adsorbing most if not all of the sulfur compounds from the feed stream. Copper containing adsorbents are also effective at taking out sulfur, especially H₂S, but are known to allow other sulfur compounds to partially or completely pass through the guard bed, including sulfides and thiophenes. Depending on the catalyst and application, the fact that some sulfur passes through a guard bed may be acceptable since sulfur is often used to moderate the downstream catalyst performance to the desired level. In general, however, thiophenes are less desirable as the sulfur form than, for example, disulfides.

In addition to adsorbents, a number of different catalysts are known in the art that are effective for removing sulfur compounds. For example, activated carbon has a high capacity for ethyl mercaptans, manganese oxide is effective for dimethyl sulfoxide removal, and zinc oxide can be used to remove hydrogen sulfide. Other catalysts known to be effective in desulfurization processes include carbon, copper / zinc oxides, nickel-based sorbents, nickel oxides, zeolites, molecular sieves and faujasites, among others. In addition, different methods have been used to reduce the sulfur level in feedstreams,

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such as prior art hydrodesulfurization (HDS) processes. These processes are usually carried out at high temperatures and pressures, so they are relatively expensive processes. Further, the HDS processes normally only reduce the sulfur content in gasoline feedstreams to levels of about 200 ppm whereas it is desirable to reduce the sulfur content to about 10 ppm. Thus, a better method for removal of unacceptable sulfur-containing compounds is needed.

Summary of the Invention

The present invention is a method for the adsorption of sulfur-containing compounds from a hydrocarbon feedstream. The method comprises contacting the sulfur-containing compound with a copper oxide / zinc oxide / aluminum oxide catalyst optionally promoted with an alkali metal, such as K, Rb, Cs, or with a metal selected from the group consisting of Ti, V, Mn, Zr, Mo, Ru, Rh, Pd, Ba, La, Re, Tl, Ce and combinations thereof, wherein the catalyst is prepared from a hydroxycarbonate precursor having from about 1% to about 60% of the catalyst aluminum intercalated in a hydrotalcite, wherein the hydrotalcite is defined as $(\text{Cu,Zn})_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, and wherein the promoter is applied so as to be accessible at the surface layer of the catalyst.

Detailed Description of the Invention

The present development is a process for improved sulfur adsorption using a copper oxide catalyst. The catalyst comprises copper oxide, zinc oxide and alumina, and optionally a promoter selected from the group consisting of Ti, V, Mn, Zr, Mo, Ru, Rh, Pd, Ba, La, Re, Tl, Ce, and an alkali metal, such as K, Rb, Cs, and combinations thereof. The catalyst is produced from a mixed metal hydroxycarbonate precursor having less than about 60% of the aluminum intercalated in hydrotalcite. The resulting catalyst has been surprisingly discovered to be a more effective sulfur adsorbent material than otherwise similar compositions disclosed in the prior art. The catalyst is similar in composition,

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physical properties and method of preparation as the water gas shift catalyst taught and claimed in U.S. Patents 6,627,572 and 6,693,057, which are incorporated herein in their entirety by reference.

Copper oxide / aluminum oxide catalysts and copper oxide / zinc oxide / alumina catalysts made by methods other than taught in the '572 and '057 patents are known in the art for sulfur adsorption. It has been surprisingly discovered herein that the copper oxide / zinc oxide / alumina catalysts made by the method taught in the '572 and '057 patents demonstrate sulfur adsorption at least two times greater than the prior art sulfur adsorbents.

The catalysts that perform as anticipated can be prepared with up to about 90% of the aluminum intercalated in hydrotalcite. In an exemplary embodiment, without limitation, from about 1% to about 60% of the aluminum is intercalated in hydrotalcite, and preferably from about 5% to about 45% of the aluminum is intercalated in hydrotalcite. For this invention, the term "hydrotalcite" is limited to ternary mixtures of copper, zinc and aluminum with the general structure of $(\text{Cu,Zn})_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$. For this invention, the term "hydrotalcite aluminum" or "HTAl" refers to the concentration of aluminum that is present in the precursor in the form of hydrotalcite divided by the total aluminum concentration of the catalyst. To prepare the desulfurization catalyst, appropriate quantities of copper salts and zinc salts are mixed with an aluminum component in an aqueous solution to produce a catalyst precursor mixture, as taught in the '572 and '057 patents.

The catalyst may be formed into any conventional product shape, such as a tablet. Preferred methods for the preparation of the catalyst shape include pelletizing or other conventional molding processes to produce catalysts, especially in the form of spheres, pellets, rings, tablets or extruded products formed mostly of solid or hollow objects in order to achieve high geometric surface with simultaneously low resistance to flow.

The chemical composition of the catalyst before reductive activation, expressed by weight percentage based on dry weight (no volatile content) after calcination is from about 5% to 70% copper oxide, from about 20% to 50% zinc oxide, and from about 5% to about 50% aluminum oxides.

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Alternatively, more preferred ranges for the materials are: the copper oxide may be present at from about 30% to about 60%, the zinc oxide at from about 20% to about 50%, and the aluminum oxide at from about 5% to about 20%.

The catalyst produced by the process as taught in the '572 and '057 patents has a surface area of from about 40 m²/g to about 200 m²/g, a copper surface area of greater than about 15 m²/g, and a pore volume of from about 0.2 cc/g to about 0.4 cc/g. Optionally, the catalyst may further comprise from about 50 ppm to about 20 wt% promoter, wherein said promoter is selected from the group consisting of potassium, cesium, rubidium, titanium, zirconium, manganese, vanadium, molybdenum, ruthenium, rhodium, palladium, barium, lanthanum, rhenium, thallium, cerium, a Group I metal, a Group IV-B metal and combinations thereof.

It has been discovered that catalysts prepared according to the '572 and '057 patents demonstrate sulfur-trapping behavior. These catalysts are particularly effective sulfur traps when the catalyst bed is held at a temperature of from about 300°F up to about 375°F, but are also effective at temperatures as low as about 250°F.

The process for sulfur adsorption involves contacting a sulfur-containing feedstream with the catalyst at a temperature of from about 250°F up to about 375°F while maintaining a pressure of from about 50 psig to about 250 psig, and preferably at about 150 psig. The feed rate may vary, and in an exemplary run the LHSV (liquid-hourly space velocity) is from about 1 per hour to about 10 per hour, and preferably from about 4 per hour to about 5 per hour.

The following information is presented for example only, and is not intended to be limiting in any way: The catalysts used in examples 1 – 7 are specified in Table I below. The physical properties of each Example catalyst is provided in Table II.

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Table I

Example	Catalyst Type	Carrier	Form	Cu wt%	Cu / Zn Ratio
1	CuO	Al ₂ O ₃	1/8" extrudate	20.4	—
2	CuO/ZnO	Al ₂ O ₃	1/16" extrudate	41.0	1.99 / 1
3	CuO/ZnO	Al ₂ O ₃	tablets	38.5	1.89 / 1
4	CuO/ZnO	Al ₂ O ₃	tablets	32.3	0.93 / 1
5	CuO/ZnO	Al ₂ O ₃	tablets	42.5	2.35 / 1
6	CuO/Mn	Al ₂ O ₃	tablets	42.2	—
7	CuO/ZnO/Mn	Al ₂ O ₃	tablets	30.3	0.78 / 1

Table II

Example	CBD (g/cc)	Packing density ^a (g/cc)	Cu surface area (m ² /g)	BET-surface area (m ² /g)	Mercury pore volume (cc/g)	Mean pore diameter (nm)
1	0.73	0.57	2.0	178.4	0.626	14.0
2	1.30	1.22	5.6	61.0	0.216	15.0
3	1.12	0.93	19	95.5	0.302	12.6
4	1.29	1.03	5.1	45.7	0.255	23.3
5	1.20	0.96	20	81.6	0.329	15.0
6	1.73	1.28	7.1	78.7	0.158	14.7
7	1.07	0.87	13.6	57.7	0.338	16.5

^a Sized 16 x 20

Example Catalysts 1 – 7 are evaluated for sulfur trapping using accelerated performance testing procedures. A dual fixed bed unit with temperatures of about 300°F, pressure of about 150 psig, LHSV of about 5 hr⁻¹ is provided with a feed stream of naphtha having about 200 ppm by weight sulfur in the form of butanethiol. Breakthrough is defined as 80% sulfur detected in feed exiting the fixed bed. The hours on stream and breakthrough time for each Example Catalyst is provided in Table III. The total sulfur pickup at breakthrough is calculated based on the total hours on stream.

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Table III

Example	Time on Stream (hrs)	Breakthrough Time, BT (hrs)	S balance (%)	Analytical data at HOS		Calculated data			
				Total S pickup (mg)	Total % S pickup (%)	at HOS		at BT	
						Total S pickup (mg)	Total % S pickup (%)	Total S pickup (mg)	Total % S pickup (%)
1	98	66	98	549.6	4.8	540.7	4.5	442.9	3.7
2	193	185	110	1278.4	5.2	1389.9	5.6	1387.2	5.6
3	214	209	114	1630.0	9.6	1860.8	10.1	1845.7	10.0
4	193	139	142	697.2	3.4	987.6	4.8	933.1	4.5
5	193	139	143	1032.8	5.7	1475.8	7.7	1397.0	7.2
6	309	289	111	1312.9	5.1	1455.2	5.7	1388.0	5.4
7	290	260	105	1386.0	7.1	1460.0	8.4	1385.0	7.9

The efficiency of these reactions seems to be dependent on the total and copper specific surface areas of the catalyst used. This is especially true for highly dispersed copper on CuO/ZnO/alumina materials.

The principals, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed or limited to the particular terms of disclosure, as these are to be regarded as being illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

REPLACEMENT PAGE

- Claim 1.** A process for the adsorption of sulfur from a hydrocarbon feedstream comprising contacting the feedstream with a catalyst at a temperature of from 250°F up to 375°F and at a pressure of from 50 psig to 250 psig and wherein the sulfur-containing feedstream contacts the catalyst at a feed rate defined in terms of LHSV and the LHSV is from 1 per hour to 10 per hour, and wherein said catalyst comprises from 5 wt% to 70 wt% copper oxide, from 20 wt% to 50 wt% zinc oxide, and from 5 wt% to 50 wt% aluminum oxide, said catalyst being prepared from a precursor material comprising aluminum, wherein from 1% to 60% of said aluminum is intercalated in a hydrotalcite, wherein said hydrotalcite is defined as $(\text{Cu,Zn})_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$.
- Claim 2.** The process of Claim 1 or Claim 19 wherein the sulfur-containing feedstream contacts the catalyst at a pressure of from 150 psig.
- Claim 3.** The process of Claim 1 or Claim 20 wherein the sulfur-containing feedstream contacts the catalyst at a feed rate defined in terms of LHSV and the LHSV is from 4 per hour to 5 per hour.
- Claim 4.** The process of Claim 1 or Claim 16 wherein said precursor comprises from 5% to 45% of said aluminum is intercalated in hydrotalcite.
- Claim 5.** The process of Claim 1 or Claim 16 wherein said catalyst further comprises from 50 ppm to 20 wt% promoter, wherein said promoter is selected from the group consisting of potassium, cesium, rubidium, titanium, zirconium, manganese, vanadium, molybdenum, ruthenium, rhodium, palladium, barium, lanthanum, rhenium, thallium, cerium, a Group I metal, a Group IV-B metal and combinations thereof.
- Claim 6.** The process of Claim 5 wherein said promoter comprises 50 ppm to 2.0 wt% of said catalyst.
- Claim 7.** The process of Claim 1 wherein said catalyst further defines a surface area and said surface area is from 40 m²/g to 200 m²/g.
- Claim 8.** The process of Claim 1 wherein said catalyst further defines a pore volume and said pore volume is from 0.2 cc/g to 0.4 cc/g.
- Claim 9.** The process of Claim 1 wherein said copper surface area is at least 15 m²/g.
- Claims 10 – 15.** (cancelled)
- Claim 16.** A process for the adsorption of sulfur from a hydrocarbon feedstream comprising contacting the feedstream with a catalyst comprising from 5 wt% to 70 wt% copper oxide, from 20 wt% to 50 wt% zinc oxide, from 5 wt% to 50 wt% aluminum oxide, said catalyst being prepared from a precursor material comprising aluminum, wherein from 1% to 60% of said aluminum is intercalated in a hydrotalcite, wherein said hydrotalcite is defined as $(\text{Cu,Zn})_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, and wherein said catalyst defines a surface area and said surface area is from 40 m²/g to 200 m²/g, and said catalyst further defines a pore volume and said pore volume is from 0.2 cc/g to 0.4 cc/g.
- Claim 17.** (cancelled).

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Claim 18 . The process of Claim 16 wherein the sulfur-containing feedstream contacts the catalyst at a temperature of from 250°F up to 375°F.

Claim 19 . The process of Claim 16 wherein the sulfur-containing feedstream contacts the catalyst at a pressure of from 50 psig to 250 psig.

Claim 20 . The process of Claim 16 wherein the sulfur-containing feedstream contacts the catalyst at a feed rate defined in terms of LHSV and the LHSV is from 1 per hour to 10 per hour.