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(54) Title: NOVEL MULTIMETALLIC SULFIDE CATALYSTS CONTAINING NOBLE METALS AND HYDRODENITROGENATION PROCESS USING SAME

(57) Abrégé/Abstract:
The present invention relates to novel catalysts for removing heteroatoms, particularly nitrogen, from hydrocarbonaceous feedstocks. The catalysts are comprised of highly dispersed molybdenum sulfide promoted with a noble metal such that the noble metal is in an oxidation state greater than 0 and coordinated to S. The noble metal is selected from Pt, Pd, Rh, and Ir. It is preferred that the catalysts of be prepared from a precursor composition selected from platinum ethoxyethyl xanthate or platinum dithiocarbamate. Additionally, the catalyst may include a promotor sulfide such as nickel sulfide, cobalt sulfide or iron sulfide, etc. or mixtures thereof.

ABSTRACT OF THE DISCLOSURE

The present invention relates to novel catalysts for removing heteroatoms, particularly nitrogen, from hydrocarbonaceous feedstocks. The catalysts are comprised of highly dispersed molybdenum sulfide promoted with a noble metal such that the noble metal is in an oxidation state greater than 0 and coordinated to S. The noble metal is selected from Pt, Pd, Rh, and Ir. It is preferred that the catalysts of be prepared from a precursor composition selected from platinum ethoxyethyl xanthate or platinum dithiocarbamate. Additionally, the catalyst may include a promotor sulfide such as nickel sulfide, cobalt sulfide or iron sulfide, etc. or mixtures thereof.

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NOVEL MULTIMETALLIC SULFIDE CATALYSTS CONTAINING NOBLE METALS AND HYDRODENITROGENATION PROCESS USING SAME

FIELD OF THE INVENTION

The present invention relates to catalysts for heteroatom removal, especially to hydrodenitrogenation catalysts for removing nitrogen from petroleum and synthetic fuel feedstocks. The catalysts are unsupported catalyst comprised of highly dispersed molybdenum sulfide, and a noble metal in an oxidation state greater than zero, preferably greater than one, and coordinated primarily to sulfur. Additionally, the catalysts may include a promoter metal sulfide, such as nickel sulfide, cobalt sulfide, iron sulfide, or a mixture thereof. It is critical that the sulfides of the various metals be intimately mixed and highly dispersed. This invention also relates to a method of preparing such catalysts from certain noble metals, molybdenum, and promoter metal complexes and a hydrodenitrogenation process for using said catalyst.

BACKGROUND OF THE INVENTION

Hydrotreating of petroleum feedstocks and various boiling fractions thereof has become increasingly important because of more stringent product quality requirements. Furthermore, the petroleum industry foresees the time when it will have to turn to relatively high boiling feeds derived from such materials as coal, tar sands, oil-shale, and heavy crudes. Feeds derived from such materials generally contain significantly more deleterious components, such as sulfur, nitrogen, oxygen, halides, and metals. Consequently, such feeds require a considerable amount of upgrading in order to reduce the content of such components, thereby making them more suitable for further processing, such as fluid catalytic cracking and/or cracking and/or catalytic reforming.

Hydrotreating is well known in the art and usually requires treating a hydrocarbonaceous feed with hydrogen in the presence of a catalyst to effect conversion of at least a portion of the feed to lower boiling products, usually with removal of deleterious components. See for example U.S. Patent No. 2,914,462 which discloses the use of molybdenum sulfide for hydrodesulfurizing gas oil and U.S. Patent No. 3,148,135 which discloses the use of molybdenum sulfide for hydrorefining sulfur and nitrogen-containing hydrocarbon oils. Further, U.S. 2,715,603 discloses the use of molybdenum sulfide as a catalyst for the hydrogenation of heavy oils, and U.S. Patent 3,074,783 discloses the use of molybdenum sulfides for producing sulfur-free hydrogen and carbon dioxide, wherein the molybdenum sulfide converts carbonyl sulfide to hydrogen sulfide. Molybdenum and tungsten sulfides have other uses as catalysts, including hydrogenation, methanation, water gas shift, etc. reactions.

In general, with molybdenum and other transition metal sulfide catalysts, as well as with other types of catalysts, greater catalyst surface areas generally result in more active catalysts than similar catalysts with lower surface areas. Thus, those skilled in the art are constantly trying to achieve catalysts having ever greater surface areas. More recently, it has been disclosed in U.S. Patent Nos. 4,243,553 and 4,243,554 that molybdenum sulfide catalysts of relatively high surface area may be obtained by thermally decomposing selected thiomolybdate salts at temperatures ranging from about 300° to 800°C in the presence of essentially inert, oxygen-free atmospheres. Suitable atmospheres are disclosed as consisting of argon, a vacuum, nitrogen, and hydrogen. In U.S. Patent No. 4,243,554, an ammonium thiomolybdate salt is decomposed at a rate in excess of 15°C per minute, whereas in U.S. Patent 4,243,553, a substituted ammonium thiomolybdate salt is thermally decomposed at a substantially slower heating rate of about 0.5 to 2°C per minute. The processes disclosed in these patents are claimed to produce molybdenum disulfide catalysts having superior properties for water gas shift and methanation reactions as well as for catalyzed hydrogenation and hydrotreating reactions.

Hydrotreating catalysts comprising molybdenum sulfide, in combination with other metal sulfides, are also known. For example, U.S. Patent No. 2,891,003 discloses an iron-chromium composition for desulfurizing olefinic gasoline fractions. Further, U.S. Patent No. 3,116,234 discloses Cr-Mo and also Mo with Fe and/or Cr, and/or Ni for hydrodesulfurization. Also, U.S. Patent No. 3,265,615 discloses Cr-Mo for hydrodenitrogenation and hydrodesulfurization.

Hydrotreating catalysts containing platinum are also known. For example, U.S. Patent No. 3,422,002 discloses hydrotreating with a catalyst consisting essentially of 0.05 to 5 wt.% of a platinum series metal and about 4 to 30 wt.% of molybdena on alumina, the catalyst having been presulfided.

While various of these catalysts have met with commercial success, there still exists a need in the art for catalysts having ever improved properties with respect to hydrodenitrogenation over those conventionally used.

SUMMARY OF THE INVENTION

In accordance with the present invention, there are provided novel catalysts for removing heteroatoms, particularly nitrogen, from hydrocarbonaceous feedstocks. The catalysts are comprised of highly dispersed molybdenum sulfide promoted with a noble metal such that the noble metal is in an oxidation state greater than 0 and coordinated primarily to S. The molybdenum sulfide can, in addition, be promoted by sulfides of one or more of metals from Ni, Co, Fe, etc.

In preferred embodiments of the present invention, the noble metal is selected from Pt, Pd, Rh, and Ir.

In other preferred embodiments of the present invention, the noble metal is platinum and is in an oxidation state greater than 1, and in an amount from about 0.1 to 10.0 wt.% of the total catalyst, with a molar ratio of platinum to molybdenum of about 0.001 to 0.10.

In still other preferred embodiments of the present invention, the amount of platinum present is about 0.25 to 5.0 wt.% of the total catalyst and the molar ratio of platinum to molybdenum is about 0.0025 to 0.05. When one or more of Ni, Co or Fe are present, the molar ratio of Ni, Co, or Fe/Mo can vary over a wide range but would generally be from 0.1 to 0.5.

In yet other embodiments of the present invention, the catalysts are prepared from: (a) one or more noble metal complexes; (b) one or more molybdenum complexes; and (c) optionally one or more soluble, or easily dispersible, complexes of Ni, Co and Fe, etc. The noble metal complexes are selected from those represented by the formula ML_2, when the noble metal is Pt or Pd; and ML_3, when the noble metal is Rh or Ir; where M is the noble metal and L is a ligand selected from dithiocarbamates, dithiophosphates, xanthates, thioxanthates, and further wherein L has organo groups having a sufficient number of carbon atoms to render the noble metal complex soluble in oil. Similarly, Ni complexes will be ML_2 and Co and Fe complexes of the type ML_3. The molybdenum complex is also oil soluble and/or highly dispersible and is selected from

$MoO_2(S_2CNR_2)_2$

where R is a C_1 to C_{18} alkyl group, a C_5 to C_8 cycloalkyl group, a C_6 to C_{18} alkyl substituted cycloalkyl group, or a C_6 to C_{18} aromatic or alkyl substituted aromatic group.

or

$Mo_2O_2(\mu\text{-}S)_2(S_2CNR_2)_2$

where R is as indicated,

or any related complex of molybdenum with dithiocarbamate, dithiophosphate, xanthates, or thioxanthate ligands.

In another preferred embodiment of the present invention, the noble metal complex is bis(2-ethoxyethylxanthato)Pt and the molybdenum complex is dioxo bis(n-dibutyldithiocarbamato)MoO_2^{VI}, sometimes herein referred to as dioxoMoDTC.

In still other preferred embodiments of the invention, the noble metal complex is bis(di-n-butyldithiocarbamato)Pt and the molybdenum complex is $Mo_2O_2(\mu\text{-}S)_2(S_2CNR_2)_2$ (R = n-butyl).

There is also provided a hydrotreating process for removing heteratoms, particularly nitrogen, from hydrocarbonaceous feedstocks by use of said catalysts.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is an electron micrograph of the catalyst of Example 4 hereof.

Figure 2 is a Pt- X-ray Photoelectron Spectrum (XPS) of the catalyst of Example 4 hereof.

Figure 3 is an Extended X-ray Absorption Fine-Structure (EXAFS) of the catalyst of Example 4 hereof.

Figure 4 is an electron micrograph of Catalyst C of Example 12 hereof which illustrates that agglomeration of Pt had occurred.

Figure 5 is an electron micrograph of Catalyst C3 of Example 12 hereof which shows no discernible Pt agglomeration.

Figure 6 is an electron micrograph of the catalyst of Example 7 hereof.

DETAILED DESCRIPTION OF THE INVENTION

A variety of feedstocks can be hydrotreated with the catalysts of the present invention, including hydrocarbonaceous fractions and whole feeds. Non-limiting examples of such feeds include organic solvents, light, middle and heavy distillates, and residual feeds.

In the practice of the present invention, a feed with a high heteroatom content, especially a high nitrogen concentration feedstream, is contacted with hydrogen at hydrodenitrogenation conditions in the presence of an unsupported slurry catalyst. The catalyst is comprised of a highly dispersed molybdenum sulfide and a noble metal such that the noble metal is in an oxidation state greater than 0, preferably greater than 1 and coordinated primarily to S. The catalyst optionally contains a sulfide of a promoter metal such as Ni, Co, or Fe. By highly dispersed, we mean that the molybdenum sulfide exists as small (<50 μm) particles which do not appear to be crystalline as measured by any conventional analytical technique, such as X-ray diffraction (XRD). These highly dispersed particles have more catalytically active sites per gram of molybdenum than larger particles do. Further, the noble metal is present in an amount from about 0.1 to about 10.0 wt.%, based on the total weight of the catalyst. Preferably, about 0.25 to about 5.0 wt.% of noble metal is present. Also, the noble metal is present in the above amount such that the molar ratio of noble metal to molybdenum is from about 0.001 to about 0.1, preferably from about 0.0025 to about 0.05. The noble metal will be coordinated primarily to sulfur of the ligands. By coordinated primarily to sulfur of the ligands, we mean that the noble metal will be in an oxidation state greater than 0, preferably greater than 1, and most preferably greater than 2. This high oxidation state will be provided by coordination with S, which can be verified by an analytical technique such as X-ray photoelectron spectroscopy (XPS) and/or Extended X-ray Absorption Fine Structure (EXAFS). Noble metals suitable for use herein include platinum, palladium, rhodium, and iridium. Preferred are platinum and rhodium, and more preferred is platinum.

The catalysts of the present invention are prepared from catalyst precursors. The noble metal precursor can be represented by:

ML_2 when M is Pt or Pd, and

ML_3 when M is Rh or Ir

where L is a ligand selected from the dithiocarbamates, dithiophosphates, xanthates, and the thioxanthates, wherein L contains organo groups having a sufficient number of carbon atoms to render the noble metal complex soluble or highly dispersed in a hydrocarbonaceous solvent or feedstock. For example, the organo group can be selected from alkyl, aryl, substituted aryl, and ether groups. Generally, the number of carbon atoms of the organo group will be from about 4 to 30. Preferred are the dithiocarbamates and the xanthates. For example, the alkoxyalkylxanthates represented by the formula:

$$(R_1\text{-O-}R_2\text{-O-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-S})_n\ M$$

where R_1 is an alkyl group (straight, branched, or cyclic); an alkoxy substituted alkyl group; an aryl group; or a substituted aryl group,

R_2 is a straight or branched alkylene group,

M is the noble metal,

n is an integer from 1 to 4, and is equal to the oxidation state of the metal

Preferably, R_1 is a straight chain alkyl group, a branched alkyl group, or an alkoxy substituted alkyl group. Most preferably, R_1 comprises a straight chained alkyl group. Although the number of carbon atoms in R_1 can vary broadly, typically R_1 will have from 1 to 24, preferably from 2 to 12, and more preferably from 2 to 8, carbon atoms. Typically, R_2 will have from 2 to 8, preferably from 2 to 4, carbon atoms. Most preferably, R_1 and R_2 will each have from 2 to 4 carbon atoms. R_1 and R_2 together should contain a sufficient number of carbon atoms such that the metal alkoxyalkylxanthate is soluble in the oil. Examples of suitable substituted groups in R_1 include alkyl, aryl, alkylthio, ester groups, and the like.

M can be a variety of metals, but, in general, will be a metal selected from the group consisting of Pt, Pd, Rh, Ru and Ir.

Examples of the various metal alkoxyalkylxanthates that can be used in the practice of the present invention are platinum bis(ethoxyethylxanthate), platinum butoxyethylxanthate, platinum propyloxyethylxanthate, platinum isopropyloxyethylxanthate, platinum

2-ethylhexyloxyxanthate, Rh trisethoxyethylxanthate, Rh trisbutoxyethyl-xanthate, Rh tris(2-ethoxyethalxanthate) etc.

Noble metal dithiocarbamates can be represented by the formula

$$\begin{matrix} R_2 \\ R_2 \end{matrix} NCS_2)_n M$$

where R_1 and R_2 can be the same or different and are selected from

C_1 to C_{16} alkyl groups, preferably C_2 to C_8 alkyl group

C_6 to C_{18} aryl or alkyl substituted aryl group

where n is equal to 2, M is Pt or Pd, when n = 3, M is Rh or Ir,

most preferred metal being Pt

The molybdenum complex is also oil soluble and oil dispersible, and can be selected from any of a large number of such complexes commonly known to be useful as lubricant additives (see for example Y. Yamamoto, et al. Wear (1986), p. 79-87, M. Umemura, et al. U.S. 4,692,256 (1987) and A. Papay, et al. U.S. 4,178,258 (1979). Preferred molybdenum complexes are those containing dithiocarbamate, dithiophosphate, xanthates, or thioxanthate ligands. Most preferred are Mo complexes selected from those represented by the formulas:

$MoO_2(S_2CNR_2)_2$

where R is a C_1 to C_{18} alkyl group, preferably for C_3 to C_{12} alkyl group; a C_5 to C_8 cycloalkyl group, a C_6 to C_{18} alkyl substituted cycloalkyl group, or a C_6 to C_{18} aromatic or alkyl substituted aromatic group

or

$Mo_2O_2(\mu\text{-}S)_2(S_2CNR_2)_2$

where R is as indicated above, and μ-S denotes a sulfide (S^{2-}) ligand bridging the two molybdenum atoms.

Ni and Co complexes can be selected from the xanthate or dithiocarbamate group given above; Ni, Co and Fe can also be selected from dithiocarbamates as given for noble metals.

Thermal decomposition of the aforesaid soluble complexes in a hydrocarbon liquid results in formation of active catalyst. Ratios of complexes can be varied over a wide range given the desired ratio of metals. Suitable hydrocarbon liquids include, but are not limited to, various petroleum and coal liquid distillate fractions such as naphtha, mid-distillate or vacuum gas oil. Pure liquids such as 1-methylnaphthalene, xylenes and tetralin can also be used. The formation of active catalysts can be carried out in an inert atmosphere or preferably under a hydrogen pressure ranging from about 100 to 3000 psig, preferably between about 500 to 1750 psig, and at temperatures between about 200°F to 480°C, preferably between about 340 TO 425°C. Ratios of solvent to catalyst precursors are not critical, but are generally chosen to be between about 3:1 to 25:1. The final catalyst is in the form of fine powder, with an average particle size of <10 μ, and surface areas, as measured by the B.E.T. method, in excess of 200 m^2/g.

A critical feature of the catalysts of this invention is the presence of the noble metal in an oxidation state of greater than zero, and preferably greater than 1, as indicated by XPS, and in a sulfur co-ordination environment, as indicated by both XPS and EXAFS studies.

Interaction of the noble metal with the molybdenum sulfide is believed to stabilize the noble metal in this higher oxidation state sulfided form, which is necessary for achieving high catalytic activity of the catalysts of the present invention. In these new materials, the noble metals are not poisoned by the high heteroatom content of the feed and thus, their activities are maintained.

In the absence of molybdenum sulfide, the noble metal is subject to reduction to the metallic state under the conditions used in hydrotreating catalysis, this reduction being most noticeable for Pt.

The stability of the noble metal sulfide is highly unexpected in view of the published tables of thermodynamic properties, such as those given in " S. R. Shatynski, Oxidation of Metals, 11 (No.6), 307 - 320 (1977)" which indicate that the Gibbs free energy of formation of PtS at 750°F and 10/1 H_2/H_2S is approximately zero. We have observed that reduction of the noble metal leads to redistribution and growth of the particles with decreased surface area. This leads to the loss of the beneficial effects of synergy between noble metal and molybdenum sulfides.

The present invention can also be practiced by introducing the catalyst precursors, either as a mixture in concentrate form, or simply as the precursor complex, into the feed just prior to, or into, the reaction zone. Under reactive conditions, the catalyst of the present invention will form in situ. That is, under hydrodenitrogenation conditions, the catalyst of the present invention will form as an unsupported slurry catalyst from the metal complexes used herein.

Heteroatom removal conditions, especially hydrodenitrogenation conditions, will vary considerably depending on such things as the nature of the feed being treated, the nature of the nitrogen being removed, the nature of the complexes being removed, the nature of the complexes employed, and the extent of conversion, if any, desired. Table I gives typical conditions for hydrodenitrogenating a naphtha boiling within a range of about 25°C to about 210°C, a diesel fuel boiling within a range from about 170°C to 350°C, a heavy gas oil boiling within a range of from about 325°C to about 475°C, a lube oil feed boiling within a range of from about 290 to 500°C, or residuum containing from about 10 percent to about 50 percent of material boiling above about 575°C.

TABLE I

Feed	Temp., °C	Pressure psig	Space Velocity V/V/Hr.	Hydrogen Gas Rate SCF/B
Naphtha	100-370	150-800	0.5 - 10	100-2000
Diesel	200-400	250-1500	0.5 - 6	500-6000
Heavy	260-430	250-2500	0.3 - 4	1000-6000
Lube Oil	200-450	100-3000	0.2 - 5	100-10,000
Residuum	340-450	1000-5000	0.1 - 2	2000-10,000

The following examples are presented to illustrate the invention and should not be considered limiting in any way.

EXAMPLE 1

Synthesis of bis(2-ethoxyethylxanthato)Pt, (PtEEX): To a magnetically stirred solution of 6.7g. of potassium 2-ethoxyethylxanthate, (KEEX) in 200 ml. of deionized water was added a filtered solution of potassium tetrachloroplatinate in 150 ml. of deionized water. The initial reddish-brown solution turned turbid and slowly a yellow precipitate separated out. The mixture was allowed to stir for three hours, the solid collected by filtration and washed well with deionized water. The solution was air dried and recrystallized from acetone-water to give 4.5g. (80% conversion) as yellow-orange crystals m. p. 83-84°C.

EXAMPLE 2

Synthesis of bis(2-ethoxyethylxanthato)Pd, (PdEEX): This compound was prepared from 9.5g. of (KEEX) and 6.52g. of potassium tetrachloropalladate according to the procedure given in Example 1. The product was obtained in 93% yield as a yellow shiny crystalline solid, m. p. 70°C.

EXAMPLE 3

Synthesis of tris(2-ethoxyethylxanthato)Rh, (RhEEX): This compound was synthesized from 1.92g. of sodium hexachlororhodium(III) and 4.2g. of KEEX according to the procedure given in Example 1. The product was obtained as a brown-orange crystalline solid, m. p. 75-76°C.

EXAMPLE 4

This example illustrates formation and characterization of an active Pt/Mo catalyst. A 300 cc. autoclave equipped with a magnadrive stirrer was set up to permit a continuous flow of hydrogen at elevated temperature and pressure. The autoclave was charged with 75 grams of coal vacuum gas oil (VGO), and then dioxo-MoDTC (3.99g.) and PtEEX (0.101g.) were added. The total amount of metals added corresponded to 1 wt.% on feed (0.75 g). The mixture was stirred at 1500 rpm, and heated to 800°F under 2000 psi H_2 and held at that temperature for 4 hours. Hydrogen flow was maintained at 320 cc per min. After the run the autoclave was allowed to cool to room temperature and the catalyst collected by filtration, washed with toluene, and dried at 110°C overnight in a vacuum desiccator.

Elemental analysis of the dried catalyst gave the following results: %Mo = 36.22, %Pt = 1.80, %S = 27.4, %C = 21.08, %H = 2.28, %N = 0.53. Analytical electron microscopy showed a highly disordered, molybdenum sulfide like structure (see Figure 1) while the PtSx particles, if present, were below this detection limit (<20Å). The

Pt-X-ray photoelectron spectrum (XPS) illustrated in Figure 2 shows the presence of Pt in an oxidized state (higher binding energy than for Pt metal). This has been confirmed by Extended X-ray Absorption Fine-Structure (EXAFS) studies, which indicate, as illustrated in Figure 3, that the majority of the Pt has sulfur as its nearest neighbors, as expected for a well dispersed Pt sulfide-like phase on molybdenum sulfide.

Liquid product from the autoclave was characterized by elemental analysis and GC distillation. Under the conditions described, 96.2% HDN and 97.8% HDS were achieved. The H/C of the product was improved to 1.290 (vs. 1.019 for the feed).

EXAMPLE 5

This example illustrates the catalytic activity for coal VGO upgrading of molybdenum sulfide alone produced *in situ* from dioxoMoDTC. The experiment was carried out by the procedure given in Example 4 above, and 2000 ppm (0.20%) of Mo was used. In this run, 69.3% HDS, 42.2% HDN and H/C ratio of the product of 1.149 were obtained.

EXAMPLE 6

The experiment given in Example 5 was repeated with the exception that 1.0% by weight of Mo alone was used on feed. Under these conditions, 87.7 HDS and 82.0% HDN were obtained and the H/C ratio of the product was 1.261.

EXAMPLE 7

This example illustrates the decomposition of PtEEX to form relatively large Pt metal particles with low catalytic activity in the absence of Mo sulfide. Catalyst formation was carried out in the same way as described in Example 4 above, except that the only precursor added to the autoclave was PtEEX (0.403g.). The catalyst recovered at the end of the run was examined by analytical electron microscopy, and as shown in Figure 4 hereof, was found to contain relatively large (>100Å diameter) dense particles, shown to be primarily Pt metal by XPS, as illustrated in Figure 2.

Liquid product from the autoclave was analyzed as in Example 4 hereof, and it was found that a relatively low activity, with 18.5% HDN, 36.0% HDS, and H/C for the product of 1.051.

Though this amount of Pt in Example 7 was four times that used in Example 4, the catalytic activity was much poorer. From these examples it is clear that (1) in the presence of molybdenum sulfide very small and highly dispersed PtS_x particles are formed; and (2) molybdenum sulfide and Pt/S_x very significantly enhance the activity of each other.

EXAMPLE 8

In this example, Mo/Ni catalysts with and without noble metals were evaluated for hydrodenitrogenation (HDN) activity. Catalyst A is a commercial catalyst designated KF840 and available from AKZO Chemicals Inc. It is comprised of about 2.5 wt.% Ni, 12.7 wt.% Mo, 6.4 wt.% P_2O_5, and has a surface area of about 135 m^2/g and a pore volume of about 0.38 cc/g. In catalysts B-E, the Mo and Ni precursors were dioxoMoDTC an NiEEX, while the noble metal precursors were PtEEX, and RhEEX. Autoclave runs were carried out as in Example 4 hereof. In catalysts B-E, the Mo to Ni ratio was kept at 3:1. Catalysts C-E contained 2000 ppm of Pt, Pd, or Rh, while Mo and Ni were 8000 ppm. The results are given in Table II below.

Table II

HDN Activity of Catalysts of this Invention

Catalyst	Catalyst Type	% HDN	H/C Ratio
A	KF840	80.5	1.264
B	Mo/Ni	84.5	1.296
C	Mo/Ni/Pt	95.0	1.344
D	Mo/Ni/Pd	61.0	1.24
E	Mo/Ni/Rh	91.4	1.285

From these results it is clear that Pt and Rh containing microcats show exceptionally high activity for HDN. In addition, PtSx shows the highest H/C Ratio indicating its unusual effectiveness for hydrogenation.

EXAMPLE 9

Table III given in this example compares the product composition obtained in Example 8 hereof. As is clear from the table, the catalysts of this invention give lower gas make (C_1-C_4) and higher 650°F$^-$ products than obtainable from KF840.

Table III

Product Composition From Catalytic Runs

Catalysts	C_1-C_4	C_1-C_2	200°C$^-$	200-340°C
(A) KF840	9.5	4.6	12.9	31.0
(B) Mo/Ni	7.2	3.45	11.6	35.7
(C) Mo/Ni/Pt	5.7	3.11	13.3	41.0
(D) Mo/Ni/Pd	6.4	3.08	11.8	42.6
(E) Mo/Ni/Rh	6.3	3.24	11.2	38.8

EXAMPLE 10

In this example, the 200-340°C cut of the product obtained in Example 8 was further examined for product quality. The results are given in Table IV.

Table IV

Product Distribution in 200-340°C Cut, HPLC Data

Catalysts	Sats	1 Ring	2 Ring	3 Ring	Aromatics Total
(A) KF840	18.3	55.1	18.1	8.5	81.7
(B) Mo/Ni	24.8	55.7	14.5	5.1	75.3
(F) Mo	17.6	56.3	17.7	8.4	82.4
(C) Mo/Ni/Pt	26.0	54.5	14.7	4.7	73.9
(D) Mo/Ni/Pd	17.4	57.0	18.2	7.6	82.8
(E) Mo/Ni/Rh	24.5	54.4	14.9	6.2	75.5

As is clear from this example the catalysts of this invention give the desired reduction in three ring aromatics and increased sats formation.

EXAMPLE 11

In this example the hydrodesulfurization activity of Catalysts A-E are compared as given for HDN in Example 8. The results are given in Table V.

Table V

HDS Activity of Catalysts of this Invention

Catalyst	% Hydrodesulfurization	H/C Ratio
(A) KF840	64.8	1.264
(B) Mo/Ni	82.3	1.296
(C) Mo/Ni/Pt	59.4	1.344
(D) Mo/Ni/Pd	77.2	1.294
(E) Mo/Ni/Rh	98.4	1.285

From Table VI it is clear that one of the catalysts of this invention Mo/Ni/Rh, shows exceptionally high HDS activity.

EXAMPLE 12

In this example a series of experiments was carried out. The catalysts contained Mo/Ni and Pt but the total metal loading was kept constant at 10,000 ppm. Thus the catalyst #3 contained 8000 ppm of Mo and Ni and 2000 ppm of Pt, while the catalyst #3c. contained 9,750 ppm Mo and Ni but only 250 ppm of Pt. The Table VI gives the results for HDS, HDN and H/C ratio. KF840 and Mo/Ni catalysts are also included for comparison.

Table VI

Catalyst	% HDS	% HDN	H/C Ratio
(A) KF840	81	65	1.264
(B) Mo/Ni	85	82	1.296
(C) Mo/Ni/Pt (2000 ppm)	59	95	1.344
Repeat of Run 3	78.7	90.7	1.334
C1 Mo/Ni/Pt (1000 ppm)	89	92	1.31
C2 Mo/Ni/Pt (500 ppm)	91	93	1.329
C3 Mo/Ni/Pt (250 ppm)	94	95.2	1.35
C4 Mo/Ni/Pt (50 ppm)	91.6	93	1.309

As is clear from the table, highly surprising and unexpected results are obtained. Thus by decreasing the Pt content in Mo/Ni environment the HDS and HDN activities increase, demonstrating an inverse relationship with Pt concentration. This trend continues until Pt concentration is reduced to 250 ppm. At 50 ppm Pt level used in C4 the activity starts dropping again. It seems that there is an optimum concentration of Pt somewhere between 500 ppm and 50 ppm. The same trend is displayed by H/C ratio. It decreases in going from 2000 ppm to 1000 ppm and then continues to increase until 50 ppm in which case it again shows a reduction.

In order to determine the reason for the highly unexpected activity behavior of these catalysts, the residues from using catalysts C and C3 were analyzed by analytical electron microscopy (AEM). It was found that Pt containing particles in catalyst C had agglomerated to give 50-125Å crystallites, (See Figure 4) while catalyst C3 showed no discernible Pt agglomeration, implying particle sizes less than 20Å (Figure 5).

EXAMPLE 13

A series of runs were conducted with different soluble Mo and Pt precursors in order to establish generality of the procedure for preparing the catalysts of this invention. Runs were conducted as in Example 4 hereof, with 1% total metals on feed, and a 19:1 wt. ratio Mo:Pt. Table VII below presents the results. Molyvan-A is a commercial Mo dithiocarbamate lubricant additive purchased from Vanderbilt Chemical Company. Molyvan-A contains about 28.8 wt.% Mo, 31.6 wt.% C, 5.4 wt.% H, and 25.9 wt.% S. SakuraLube-500 is a different (more soluble) Mo dithiocarbamate containing lubricant additive, obtained from Asahi Denka Corporation. SakuraLube-500 is comprised of about 20.2 wt.% Mo, 43.8 wt.% C, 7.4 wt.% H, and 22.4 wt.% S. PtDTC is bis-di-n-butyldithiocarbamato Pt (II) prepared by published literature procedures.

Table VII

Precursors	% HDS	% HDN	H/C
DioxoMoDTC/PtEEX	97.8	96.2	1.290
Molyvan-A/PtEEX	97.6	95.3	1.284
SakuraLube-500/PtEEX	98.3	95.7	1.293
SakuraLube-500/PtDTC	97.30	97.4	1.328

EXAMPLE 14

A series of runs were conducted with varying ratios of PtEEX and dioxoMoDTC. Runs were conducted as in Example 4, with 1% total metals on feed. Table VIII presents the results of these runs.

Table VIII

Pt/Mo Ratio (wt/wt)	% HDS	% HDN	H/C
0.005	93.6	90.5	1.274
0.026	97.0	94.0	1.316
0.053	96.0	95.8	1.347
0.25	89.7	98.5	1.450

Different runs in this example clearly establish that Pt/Mo combination is not limited to a certain ratio and is very active for upgrading over a very wide range.

EXAMPLE 15

A series of runs were carried out with a Pt, Mo, Co; and Pt, Mo, Co and Ni precursors for upgrading of coal VGO. Runs were conducted as in Example 4, with 1% total metals on feed. Table IX presents results of these runs.

Table IX

Metals ppm							
Mo	Pt	Ni	Co	% HDS	% HDN	H/C	Run #
7855	500	0	1615	91.0	94.9	1.322	101
7855	500	250	1365	95.6	94.8	1.376	279
8093	250	256	1401	91.6	92.6	1.325	283
8176	150	259	1415	90.4	92.9	1.312	285
8217	100	261	1422	91.3	92.0	1.297	290
8093	250	158	1499	89.9	92.8	1.295	291
8093	250	78	1579	91.1	92.5	1.283	292
8093	250	458	1199	91.3	94.4	1.323	293
8093	250	658	999	91.1	93.7	1.315	294
8093	250	958	699	86.5	93.3	1.301	295
8093	250	1158	499	88.8	94.1	1.307	296

It is clear from the table that relative ratios of the meals can be changed over a wide range and sill give catalysts which are very active for upgrading heavy feeds.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A catalyst composition comprised of highly dispersed molybdenum sulfide promoted with a noble metal such that the noble metal is in an oxidation state greater than 0 and coordinated to S.

2. The catalyst composition of claim 1 wherein the noble metal is selected from Pt, Pd, Rh, and Ir.

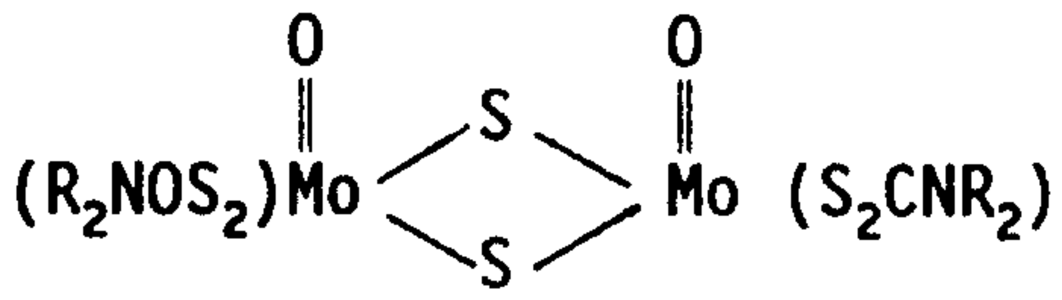
3. The catalyst composition of claim 2 wherein the noble metal is present in an amount ranging from about 0.1 to 10.0 wt.%, based on the total weight of the catalyst and is present in a molar ratio of noble metal to molybdenum of from about 0.00 to 0.1.

4. The catalyst composition of claim 2 wherein a sulfide of a second group of metals is present, said second group of metals being selected from the group consisting of Fe, Ni, and Co and wherein the ratio of said second group of metals to molybdenum is from about 0.1 to 0.5.

5. The catalyst composition of claim 2 which is prepared from a precursor comprised of: (a) one or more noble metal complexes; (b) one or more molybdenum complexes; and (c) optionally one or more soluble or easily dispersible complexes of Ni, Co, and Fe.

6. The catalyst composition of claim 5 wherein the noble metal complex is selected from those represented by the formula ML_2, when the noble metal is Pt or Pd; and ML_3, when the noble metal is Rh or Ir, where M is the noble metal and L is a ligand selected from dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, and further wherein L has organo groups having a sufficient number of carbon atoms to render the noble metal complex soluble in oil.

7. The catalyst composition of claim 6 wherein the molybdenum complex is also oil soluble and highly dispersible and is selected from the compositions represented by the formulae:

 and $MoO_2(S_2CNR_2)_2$

where R is a C_6 to C_{18} alkyl group, a C_5 to C_8 cycloalkyl group, a C_6 to C_{18} alkyl substituted cycloalkyl group, or a C_6 to C_{18} aromatic or alkyl substituted aromatic group.

8. The catalyst composition of claim 7 wherein the noble metal complex is bis(2-ethoxyethylxanthato)Pt and the molybdenum complex is dioxo bis(n-dibutyldithiocarbamato)Mo^{VI}.

9. A process for removing heteratoms from a hydrocarbonaceous feedstock which process comprises treating the feedstock at hydrotreating conditions, in the presence of hydrogen, with a catalyst composition represented by any one of claims 1 to 8.

FIG. 1

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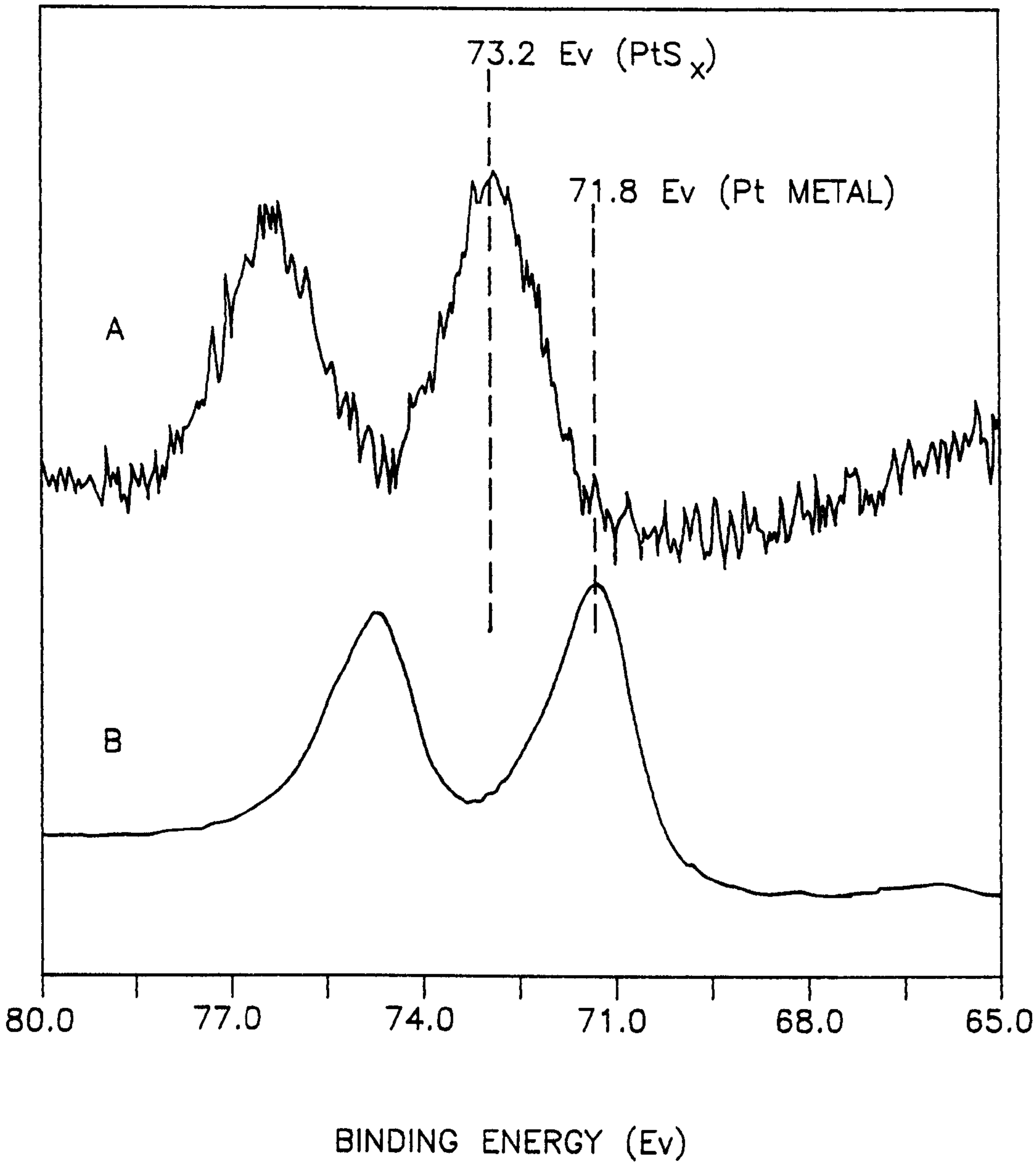

X-RAY PHOTOELECTRON SPECTRA. CURVE A IS THE CATALYST OF EXAMPLE 4. CURVE B IS THE CATALYST FROM EXAMPLE 7.

FIG. 2

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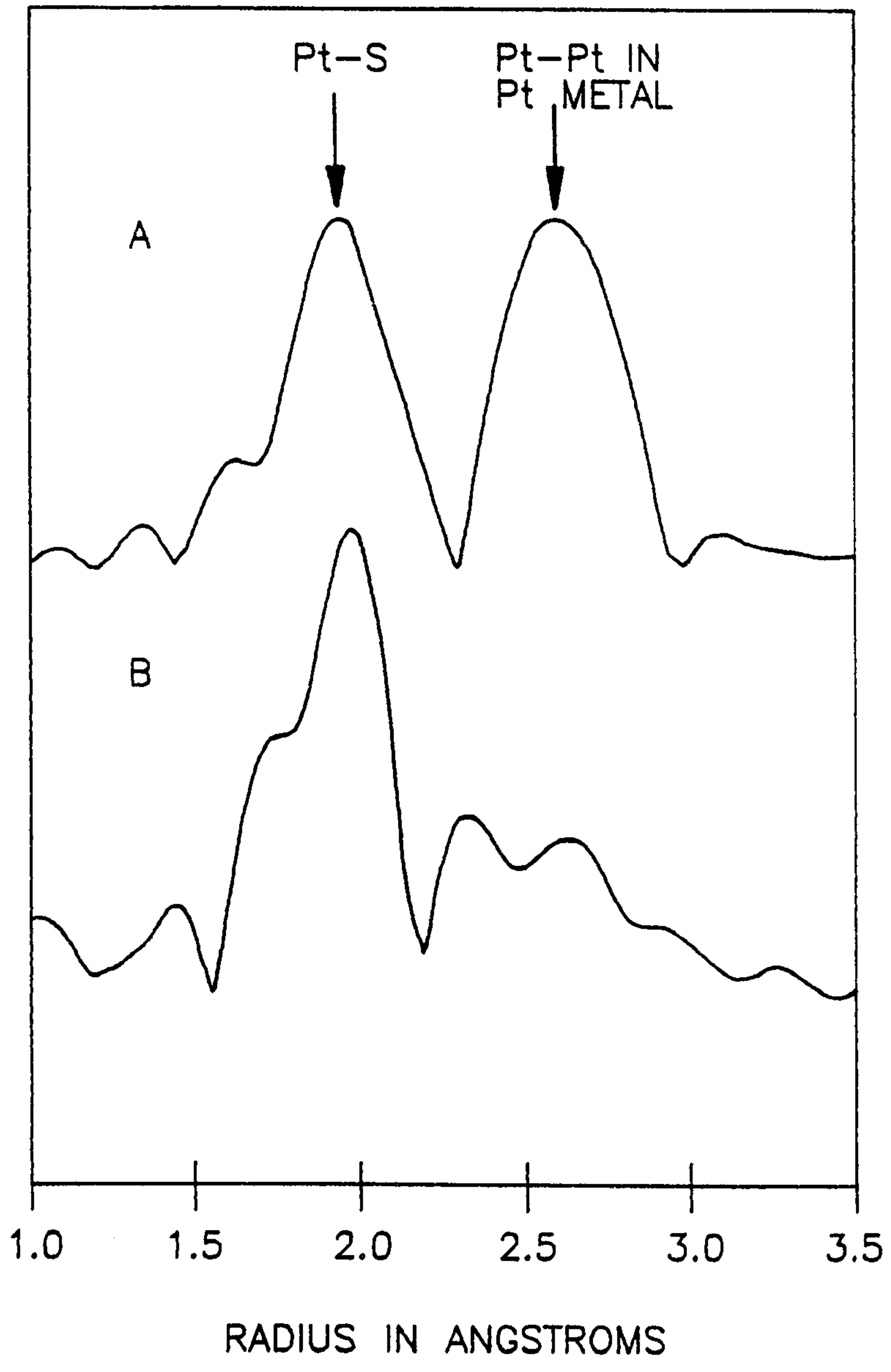

RADIAL STRUCTURE FUNCTIONS AT PT, FROM EXTENDED X–RAY ABSORPTION FINE STRUCTURE (EXAFS) SPECTRA. CURVE A IS A SIMULATED 1:1 MIXTURE OF PT SULFIDE AND PT METAL. CURVE B IS THE CATALYST OF EXAMPLE 4.

FIG. 3

Scott J. Aylen

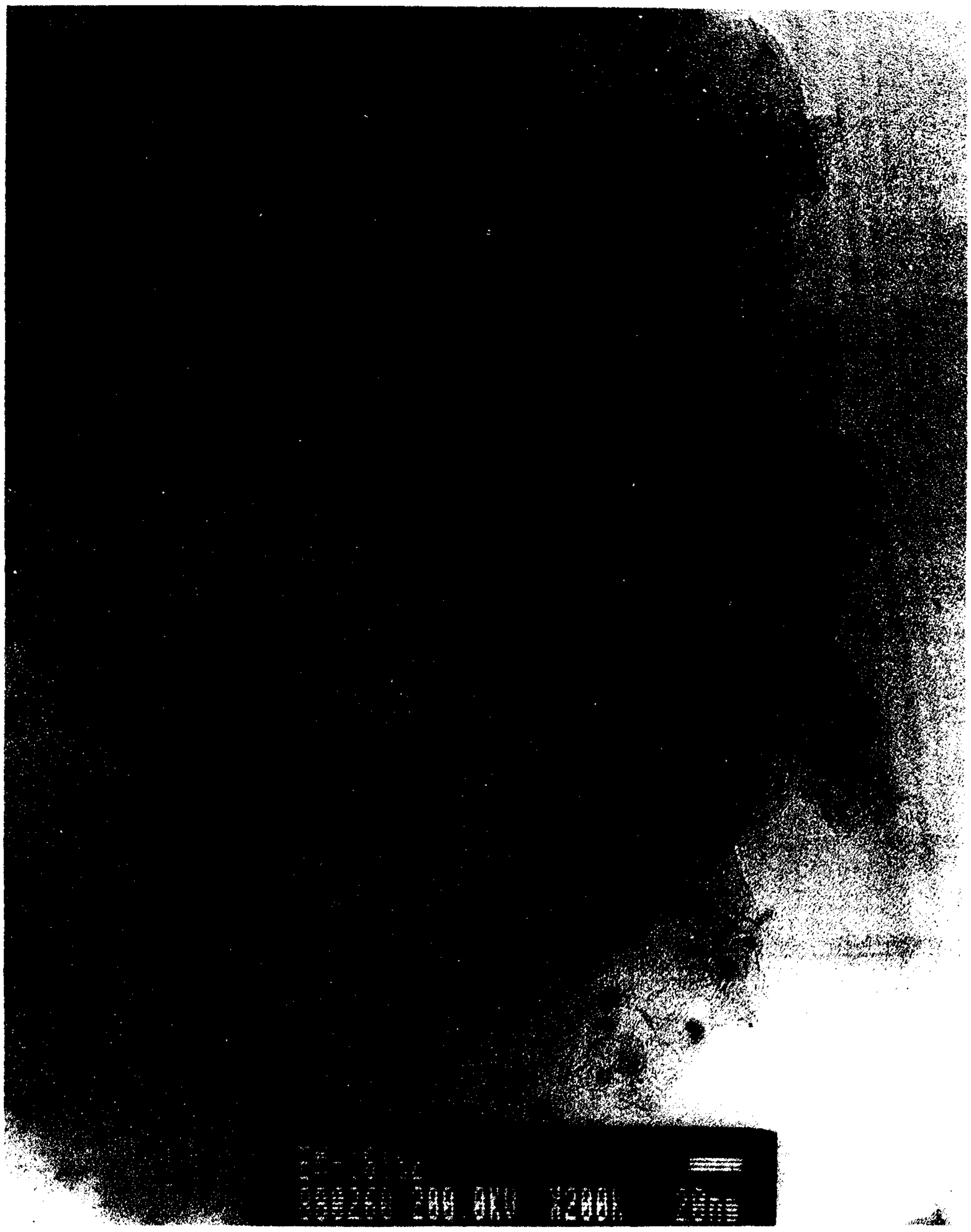

FIG. 4

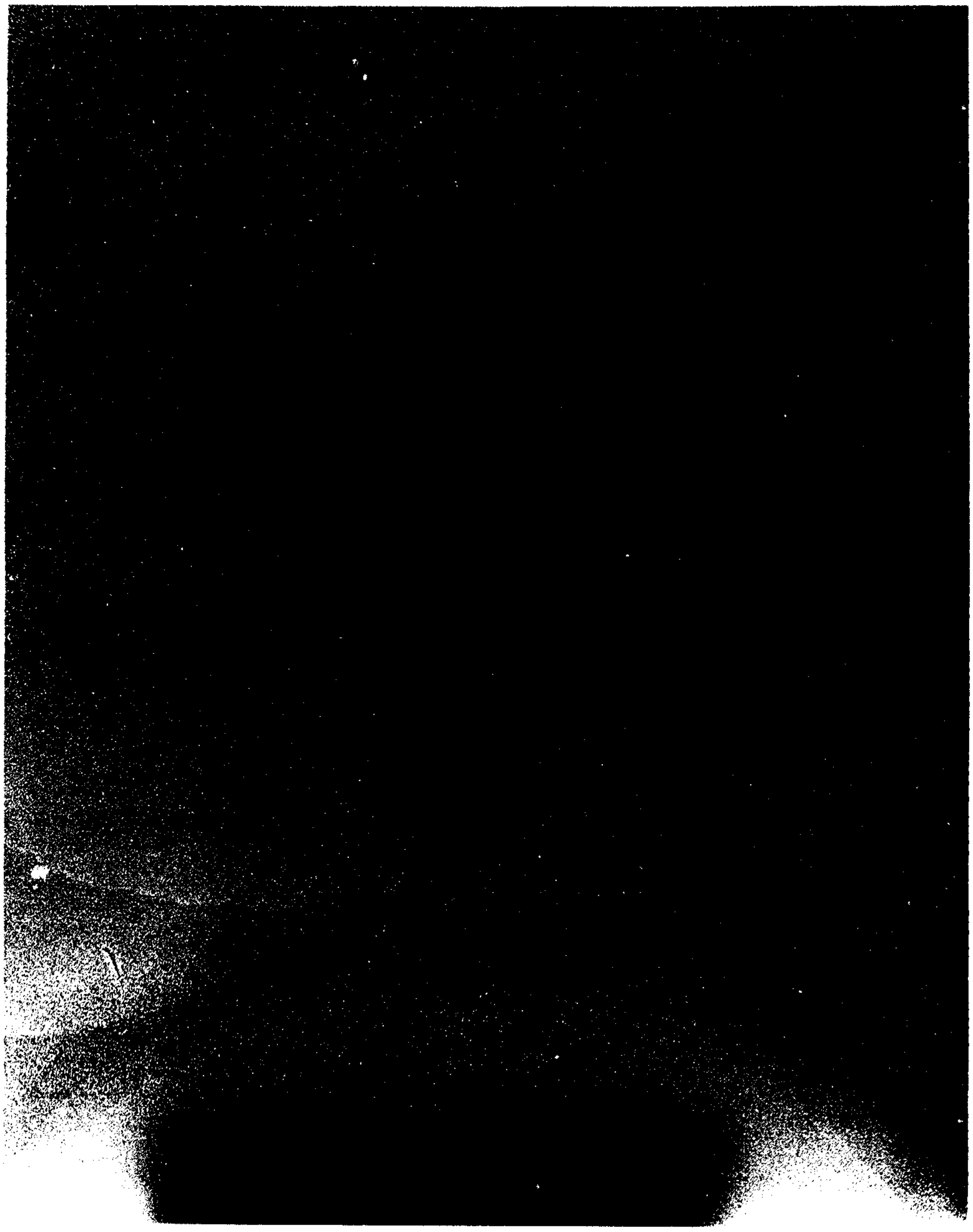

FIG. 5

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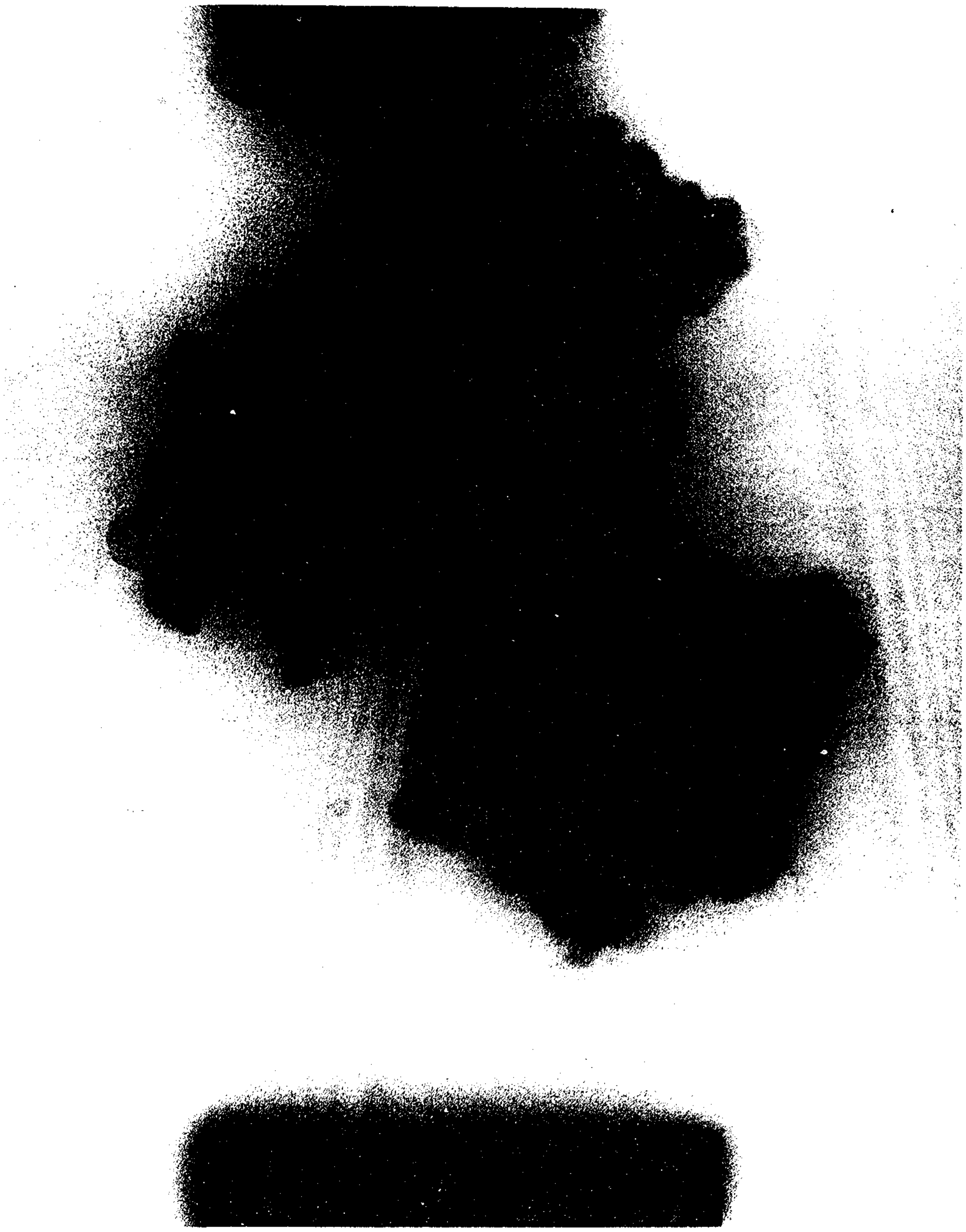

FIG. 6

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