



EUROPEAN PATENT APPLICATION

Application number : **92308168.1**

Int. Cl.⁵ : **C10G 1/08**

Date of filing : **09.09.92**

Priority : **09.09.91 US 756680**

Date of publication of application :
17.03.93 Bulletin 93/11

Designated Contracting States :
BE DE FR GB IT NL

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Coal liquefaction process.

The present invention relates to a catalytic process for converting coal to normally liquid and gaseous products, preferably liquid products. 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.

FIELD OF THE INVENTION

The present invention relates to a catalytic process for converting coal to normally liquid and gaseous products, preferably liquid products. 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.

BACKGROUND OF THE INVENTION

The petroleum industry has long been interested in the production of "synthetic" liquid fuels from non-petroleum solid fossil fuel sources. It is hoped that economic non-petroleum sources of liquid fuel will help the petroleum industry to meet growing energy requirements and decrease dependence on foreign supplies.

Coal is the most readily available and most abundant solid fossil fuel, others being tar sands and oil shale. The United States is particularly richly endowed with well distributed coal resources. Additionally, in the conversion of coal to synthetic fuels, it is possible to obtain liquid yields of about three to four barrels per ton of dry coal, or about four times the liquid yield/ton of other solid fossil fuels such as tar sands or shale, because these resources contain a much higher proportion of mineral matter.

Despite the continued interest and efforts of the petroleum industry in coal hydroconversion technology, further improvements are necessary before it can reach full economic status. Maximizing the yield of coal liquids is important to the economics of coal hydroconversion.

SUMMARY OF THE INVENTION

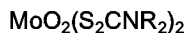
In accordance with the present invention, there is provided a process for converting coal to primarily liquid products which process comprises contacting the coal at coal liquefaction conditions with a catalysts comprised of highly dispersed molybdenum sulfide promoted with a noble metal such that the 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 0.05 to 25.0 wt.% of the total catalyst, with a molar ratio of platinum to molybdenum of about 0.0002 to 0.2.

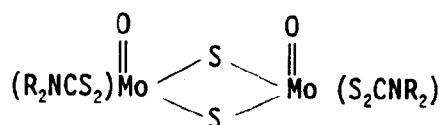
In still other preferred embodiments of the present invention, the amount of platinum present is about 0.25 to 5.0 wt.% of the total catalyst and the molar ratio of platinum to molybdenum is about 0.001 to 0.04. When one or more of Ni, Co or Fe are present, the molar ratio of Ni, Co, or Fe/Mo can vary 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 or easily dispersible 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:



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



and $\text{MoO}_2(\text{S}_2\text{CNR}_2)_2$

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.

In another preferred embodiment of the present invention, the noble metal complex is bis(2-ethoxyethyl-xanthato)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 $\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNR}_2)_2$ (R = n-butyl).

10 DETAILED DESCRIPTION OF THE INVENTION

The term "coal" is used herein to designate a normally solid carbonaceous material including all ranks of coal below anthracite, such as bituminous coal, sub-bituminous coal, lignite, peat, and mixtures thereof. The sub-bituminous and lower ranks of coal are particularly preferred. It is preferred that the coal first be reduced to a particulate, or comminuted form. The coal is suitably ground or pulverized in a conventional ball mill to provide particles of a size ranging from about 10 microns up to about 1/4 inch in diameter, typically about 8 mesh (Tyler).

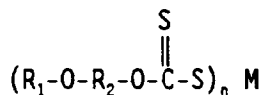
In the practice of the present invention, coal converted under liquefaction conditions in the presence of an unsupported slurry catalyst. The catalyst is comprised of a highly dispersed molybdenum sulfide and a noble metal such that the noble metal is in an oxidation state greater than 0, preferably 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 (<500 nm) 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 0.05 to about 25.0 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 0.0002 to about 0.2, preferably from about 0.001 to about 0.04. The noble metal will be coordinated primarily to sulfur. By coordinated primarily to sulfur, 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:



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

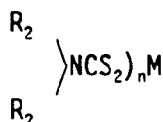
Preferably, R_1 is a straight chain alkyl group, a branched alkyl group, or an alkoxy substituted alkyl group. Most preferably, R_1 comprises a straight chained alkyl group. Although the number of carbon atoms in R_1 can vary broadly, typically R_1 will have from 1 to 24, preferably from 2 to 12, and 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 propoxyethylxanthate, platinum isopropoxyethylxanthate, platinum 2-ethylhexyloxyxanthate, Rh trisethoxyethylxanthate, Rh trisbutoxyethylxanthate, Rh tris(2-ethoxyethylxanthate) etc.

Noble metal dithiocarbamates can be represented by the formula



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

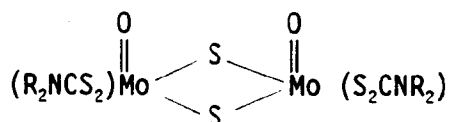
where n is equal to 2, M is Pt or Pd, when n = 3, M is Rh or Ir, most preferred metal being Pt.

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:



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



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.

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 the solvent or coal 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 250 to 2500 psig, preferably between about 500 to 1750 psig, and at temperatures between about 200° C 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. During the preparation of the active catalyst, a source of sulfur such as elemental sulfur, CS_2 , H_2S , mercaptan and organic sulfides, etc. can be included. The final catalyst is in the form of fine powder, with an average particle size of <500 nm, and surface areas, as measured by the B.E.T. method, in excess of 200 m²/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 coordination 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 leading to its poisoning and less activity.

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 H₂/H₂S 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 should lead 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 liquefaction solvent, or directly into, the reaction zone. Under reactive conditions, the catalyst of the present invention will form in situ. That is, under liquefaction conditions, the catalyst of the present invention will form as an unsupported slurry catalyst from the metal complexes used herein.

The coal is converted, or liquefied, in accordance with the present invention by introducing the coal into a liquefaction zone in the presence of a suitable solvent and the previously described catalyst. The solvents employed are solvents which may contain anywhere from 1/2 to about 2 weight % donatable hydrogen, based on the weight of the total solvent. Preferred solvents include coal derived liquids such as coal vacuum gas oils (VGO) and coal distillates or mixture thereof, for example, a mixture of compounds having an atmospheric boiling point ranging from about 175° C to about 600° C, more preferably ranging from about 340° C to less than about 540° C. Other suitable solvents include aromatic compounds such as alkylbenzenes, alkyl-naphthalenes, alkylated polycyclic aromatics, heteroaromatics, unhydrogenated or hydrogenated creosote oil, tetralin, immediate product streams from catalytic cracking of petroleum feedstocks, shale oil, or virgin petroleum streams such as vacuum gas oil or residuum, etc. and mixtures thereof. In addition, the 540° C⁺ bottoms are also recycled to the liquefaction zone.

The preferred catalyst particles, containing a metal sulfide in a hydrocarbonaceous matrix formed within the process, are uniformly dispersed throughout the feed. Because of their ultra small size, 0.002 to 3 microns, there are typically several orders of magnitude more of these catalyst particles per cubic centimeter of oil than is possible in an expanded or fixed bed of conventional catalyst particles. The high degree of catalyst dispersion and ready access to active catalyst sites affords good reactivity control of the reactions.

The catalyst loading is flexible, ranging from parts per million (ppm) to weight percents (the latter limited by pumping constraints in a slurry reactor). Higher catalyst loadings increase conversion to low boiling liquids, and decrease heteroatom content, with better selectivity to liquid over gas. The catalyst may be used in the slurry mode or, with an essentially ash free extract, in a fixed bed. Conditions may be varied to produce a more or less saturated/hydrocracked product suitable as (or for conversion to) diesel or mogas, respectively. Mild hydroconversion temperatures in the range of 340 to 425° C are preferably used.

Normal catalyst loadings on the order of 1000 ppm, ranging from 100 to 5000 ppm, are suitable for the hydroconversion reaction system of the present process. The oil-soluble metal-containing compound make-up (not including additional amounts from recycle) is added in an amount sufficient to provide from about 10 to less than 5000 wppm, preferably from about 25 to 950 wppm, more preferably, from about 50 to 700 wppm, most preferably from about 50 to 400 wppm, of the oil-soluble metal compound, calculated as the elemental metal, based on the weight of coal. Catalyst make-up rates are suitably from about 30 ppm to 500 ppm on coal. The remainder will normally be supplied from recycling the catalyst-containing 340° C⁺ bottoms.

Various methods can be used to convert a catalyst precursor, in the coal-solvent-bottoms slurry, to an active catalyst. It is usually better to form the catalyst after dissolving the soluble precursor in order to obtain better dispersion. One method of forming the catalyst from the precursor or oil-soluble metal compound is to heat in a premixing unit prior to the hydroconversion reaction, the mixture of metal compound, coal extract and solvent to a temperature ranging from about 260° C to about 450° C and at a pressure ranging from about 250 to about 2500 psig, in the presence of a hydrogen-containing gas. A sulfur-containing reagent such as H₂S, CS₂ (liquid), or elemental sulfur can also be introduced. The hydrogen-containing gas may be pure hydrogen but will generally be a hydrogen stream containing some other gaseous contaminants, for example, a hydrogen-containing stream produced from the effluent gas in a reforming process.

If H₂S is employed as the source of sulfur to activate the catalyst, then the hydrogen sulfide may suitably comprise from about 1/2 to about 10 mole % of the hydrogen-containing gas mixture. Hydrogen sulfide may be mixed with hydrogen gas in an inlet pipe and heated up to reaction temperature in a preheater, or may be part of the recycle gas stream. High sulfur coals may not require an additional source of sulfur. The catalyst

precursor treatment is suitably conducted for a period ranging from about 5 minutes to about 2 hours, preferably for a period ranging from about 10 minutes to about 1 hour, depending on the composition of the coal and the specific catalyst precursor used.

Another method of converting a catalyst precursor or oil-soluble metal compound to a catalyst for use in the present process is to react the mixture of metal compound, coal extract and solvent with a hydrogen-containing gas in the hydroconversion zone, itself at coal hydroconversion conditions.

Although the oil-soluble metal compound (catalyst precursor) is preferably added to a solvent, and the catalyst formed within the mixture of coal and solvent, it is also possible to add already formed catalyst to the solvent, although as mentioned above, the dispersion may not be as good.

In any case, a mixture of catalyst, solvent, bottoms, and coal is sent to the liquefaction zone which will now be described. The coal liquefaction zone is maintained at a temperature ranging from about 340° to 510° C, preferably from about 340° to 450° C, more preferably from between about 385° and 425° C, and a hydrogen partial pressure ranging from about 500 psig to about 5000 psig, preferably from about 1200 to about 3000 psig. The space velocity, defined as the volume of the coal, bottoms, and solvent feedstock per hour per volume of reactor (V/H/V), may vary widely depending on the desired conversion level. Suitable space velocities may range broadly from about 0.1 to 10 volume feed per hour per volume of reactor, preferably from about 0.25 to 6 V/H/V, more preferably from about 0.5 to 2 V/H/V.

The 540° C⁺ bottoms from the liquefaction zone may be recycled, in part, back to the liquefaction zone, if desired, to increase conversion by bottoms reaction to extinction. The bottoms which are purged are preferably gasified, for example by partial oxidation, along with the residue from the extraction, to produce hydrogen, carbon monoxide and heat. With bottoms recycle, a suitable solvent:coal:bottoms ratio by weight to the hydroconversion zone will be within the range of about 2.5:1:0 to about 0.5:1:2.5. Reducing the solvent to solids ratio improves the thermal efficiency of the process because the reactor size is reduced for a given coal throughput, or allows for more throughput.

The range of process conditions recommended for the liquefaction stage, according to an embodiment considered the best mode, is summarized in Table 1 below:

TABLE 1

Variable	Broad Range	Preferred Range
Liquefaction Temp., °C	340 - 510	385 - 450
Pressure, psig	500 - 5000	1200 - 3000
Slurry, Residence Time, Min.	25 - 480	60 - 240
Solvent/Coal Ratio, by Wt.	0.5 - 2.5	0.8 - 1.2
Bottoms/Coal Ratio, by Wt.	0 - 2	0 - 1.5
H ₂ Treat, Wt.% on Coal	4 - 12	6 - 10
Sulfur on Coal, Wt.%	0 - 10	0 - 4
Solvent Boiling Range, °C	175 - 600	340 - 540
Catalyst Metal on Coal, wppm	100 - 100,000	100 - 20,000

A conversion of greater than 70% to various products based on wt% DAF (dry-ash-free) coal is achieved. As noted above, however, the novel catalyst combination can offer significant improvements, for example, better liquids selectivity and conversion with a corresponding decrease in gas yield.

The process of the invention may be conducted either as a batch or as a continuous type process. Suitably, there are on-site upgrading units to obtain finished products, for example transportation fuels.

The following examples illustrate certain preferred embodiments and advantages of the present process. The examples are not intended to limit the broad scope of the invention. Further, other advantages and embodiments of the present invention will be apparent to those skilled in the art from the description provided

here.

EXAMPLE 1

5 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
10 to give 4.5g. (80% conversion) as yellow-orange crystals m. p. 83-84° C.

EXAMPLE 2

15 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

20 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

25 Preparation of bis(dibutylthiocarbamate)Pt, PtDTC: To a stirred solution of sodium dibutylthiocarbamate prepared from 37.4 g of dibutylamine, 11.4g of NaOH, 24.0 ml of carbon disulfide and 100 ml of deionized water on an ice bath, was added a solution of 40.192g of potassium tetrachloroplatinum(II) in 400 ml of deionized water under nitrogen blanket. The mixture was allowed to stir overnight and the resulting solid was collected by filtration, washed with 150 ml of deionized water and then dried under vacuum for 2 hours. It was
30 recrystallized from acetone to give bright yellow crystalline solid, 56.28g (96.7% conversion), melting point, 133° C.

Analysis calculated for $C_{18}H_{36}N_2S_4Pt$:

C, 35.82; H, 5.97; S, 21.23; Pt, 32.33.

35 Found: C, 35.83; H, 5.48; S, 21.40; Pt, 31.66.

EXAMPLE 5

40 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 groups of coal vacuum gas oil (VGO), and then di oxo-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 425° C 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
45 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 while the PtSx particles, if present, were below this detection limit (<20Å). The Pt-X-ray photoelectron spectrum (XPS) 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 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
55 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 6

In this example a series of runs were completed with an Illinois #6 coal in a bench 380 cc stirred autoclave unit. In each run, the particle size of the coal was -100 mesh. In each of the series of runs, a slurry was prepared containing 39 weight percent coal and 1000 ppm of metal as molybdenum, platinum or the mixture of the two based on dry coal. Molybdenum was used as the complex in molybdenum dioxodithiocarbamate and platinum was as platinum ethoxyethylxanthate (Pt-EEX), $(C_2H_5OCH_2CH_2OCS_2)_2Pt$. In each run, the liquefaction was accomplished at 425° C, 2300 psig constant pressure and with a nominal residence time of 150 minutes. The autoclave was agitated at 1500 rpm to promote the hydrogen transfer from the gas phase to the liquid phase. Molecular hydrogen was initially added to the liquefaction reactor in an amount of 7 weight percent based on dry coal, the hydrogen was continuously added to the autoclave as it was consumed. This gives a total hydrogen treat for about 9 wt% on dry coal. In each run, a solvent having an initial boiling point of 260° C and a final boiling point of 540° C was used. The coal conversion and C₁-C₄ gas yield for each run is summarized below:

Mo, PPM	1000	950	900	750	500	0
Pt, PPM	0	50	100	250	500	1000
Conversion, Wt% DAF	59	67	70	70	69	56
C ₁ -C ₄ , Wt% DAF	8.7	8.4	7.1	6.6	6.4	7.6
Gas Selectivity, %	14.7	12.5	10.1	9.4	9.3	13.6

The coal conversion was determined by distillation at 540° C. From the foregoing it is believed apparent that coal conversion is promoted with small amount of Pt, and C₁-C₄ selectivity is also improved. The C₁-C₄ gas selectivity is defined as C₁-C₄ divided by conversion and multiplied by 100. It is also evident that Pt-alone at 1000 PPM is not as good as any of the Pt promoted Mo cases.

EXAMPLE 7

In this example, a series of runs were completed at the same conditions in the same stirred autoclave as in Example 1, except, in each run, the liquefaction was performed at 840° F for a nominal residence time of 60 minutes. The coal conversion and C₁-C₄ gas yield for each run is summarized below:

Mo, PPM	1000	950	750	500	0
Pt, PPM	0	50	250	500	1000
Conversion, Wt% DAF	62	65	68	65	60
C ₁ -C ₄ , Wt% DAF	10.0	8.8	8.7	10.8	10.9
Gas Selectivity, %	16.1	13.5	12.8	16.6	18.2

From the foregoing it is apparent that coal conversion is promoted with a small amount of Pt, and C₁-C₄ selectivity is also improved with the promotion of Pt. However, when Pt is greater than 25% in the mixture of Pt/Mo the promotion effect becomes less effective.

EXAMPLE 8

In this example a series of runs were completed with an Illinois #6 coal in the same autoclave at the same liquefaction conditions, except the total metal for each run is at 5000 ppm in stead of 1000 ppm as in Examples 1 and 2. In each run, the liquefaction was accomplished at 450° C for a nominal residence time of 60 minutes. The coal conversion and C₁-C₄ gas yield for each run is summarized below:

	Mo, PPM	5000	4950	4900	4750	4500	4000	2500
	Pt, PPM	0	50	100	250	500	1000	2500
5	Conversion, Wt% DAF	65	71	74	74	76	75	73
	C ₁ -C ₄ , Wt% DAF	9.5	9.3	9.1	8.9	9.1	9.3	10.0
	Gas Selectivity, %	14.6	13.1	12.3	12.0	12.0	12.4	13.7

10 From the foregoing it is believed apparent that coal conversion is promoted more with smaller amount of Pt, and C₁-C₄ selectivity is also improved at the lower level of Pt.

EXAMPLE 9

15 In this example two comparable runs were completed with an Illinois #6 coal in a bench 380 cc stirred autoclave unit. The experimental conditions were similar to example 1 except the liquefaction was carried out at 370° C for a nominal residence time of 4320 minutes. Run 1 contained 1000 PPM Mo as Molybdenum dioxodithiocarbamate and Run 2 contained 750 PPM Mo as Molybdenum dioxodithiocarbamate and 250 PPM Pt as Pt-EEX. The comparable liquefaction yields and conversions are shown below:

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	Run	1	2
25	Catalyst Type,	Mo	Mo/Pt
	Concentration, ppm	1000 ppm	750/250 ppm
	C ₁ -C ₄ , Wt% DAF	7.4	5.5
	C ₅ -200° C, Wt% DAF	9.4	36.0
30	200-340° C, Wt% DAF	13.3	37.9
	340-540° C, Wt% DAF	27.8	-10.4
	540° C+ Bottoms, Wt% DAF	38.8	26.8
35	H ₂ Consumption, Wt% DAF	8.2	9.9
	Gas Selectivity, %	12.0	7.5
	Naphtha Selectivity, %	15.3	49.2
40	Conversion, Wt% DAF	61.2	73.2

45 From the foregoing table it is apparent that the use of Pt in addition to increasing conversion but also changes the selectivity dramatically to more desirable products. The improvement in conversion (12 wt%) and gas selectivity (4.5%) are obvious. However, more noteworthy are the changes in liquid products. The use of Pt dramatically shifts the product from vacuum gas oil (VGO, b. p. 340-540° C) (27.8% vs -10.4%) to the more desirable and valuable naphtha and distillate.

Claims

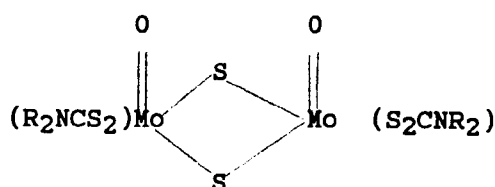
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1. A coal liquefaction process wherein coal is converted to liquid and gaseous products by heating the coal to a temperature from about 340°C to 510°C in the presence of hydrogen, a solvent and recycled bottoms and which comprises using a catalyst composition during the heating step, wherein the catalyst composition is comprised of: highly dispersed molybdenum sulfide promoted with a noble metal selected from the group consisting of Pt, Pd, Rh, Ru and Ir, such that the noble metal is in an oxidation state greater than zero and coordinated primarily to sulfur, and in the substantial absence of tin or iodine or both.
2. The process of claim 1 wherein the noble metal is present in an amount ranging from about 0.05 to 25.0

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wt%, based on the total weight of the catalyst.

3. The process of claim 1 or claim 2 wherein the molar ratio of noble metal to molybdenum is from about 0.0002 to 0.2.
4. The process of any one of claims 1 to 3 wherein the noble metal is platinum and is present in an amount of 0.25 to 5.0 wt% and the ratio of platinum to molybdenum is about 0.0001 to 0.04.
5. The process of any one of claims 1 to 4 wherein a sulfide of a second group of metals is present, the said second group of metals is selected from the group consisting of Fe, Ni, and Co.
6. The process of claim 5 wherein the ratio of said second group of metals to molybdenum is from about 0.1 to 0.5.
7. The process of any one of claims 1 to 6 wherein said catalyst is derived from a precursor comprised of:
 - (a) one or more noble metal complexes 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, xanthates, thioxanthates, dithiophosphates, and further wherein L has organo groups having a sufficient number of carbon atoms to render the noble metal complex soluble in oil or easily dispersible; and
 - (b) a molybdenum complex which is oil soluble, or highly dispersible, and is selected from the compositions represented by the formulae:



and $\text{MoO}_2(\text{S}_2\text{CNR}_2)_2$

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.

8. The process 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. The process of claim 7 or claim 8 wherein said catalyst further comprises at least one soluble or easily dispersible complex selected from the group consisting of Ni, Co, and Fe.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8168

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-1 845 439 (STANDARD I.G.) ---		C10G1/08
A	FR-A-728 913 (I.G. FARBEN) ---		
A	US-A-5 026 475 (EXXON) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 JANUARY 1993	Examiner OSWALD DE HERDT
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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