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(54) Title: PROCESS FOR PRODUCING ALCOHOLS FROM CARBON MONOXIDE AND HYDROGEN USING AN ALKALI-MOLYBDENUM SULFIDE CATALYST (57) Abstract Process for producing, selectively, predominantly C ₁ - C ₅ linear, primary alcohols by reacting carbon monoxide and hydrogen in the presence of a solid catalyst consisting essentially of molybdenum sulfide and at least about 0.20 mole, per mole of molybdenum, of an alkali metal compound, at a gas hourly space velocity of at least about 3.000 hr ⁻¹ .		

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TITLE OF THE INVENTION

PROCESS FOR PRODUCING ALCOHOLS FROM
CARBON MONOXIDE AND HYDROGEN USING AN
ALKALI-MOLYBDENUM SULFIDE CATALYST

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a catalytic process for producing alcohols directly from carbon monoxide and hydrogen; and more particularly and in a preferred embodiment to the use of an alkali-containing molybdenum sulfide heterogeneous catalyst for selectively converting carbon monoxide and hydrogen to alcohols.

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Description of the Prior Art

It is known that carbon monoxide and hydrogen may be reacted over a suitable catalyst to produce hydrocarbons and oxygenated compounds (such as aldehydes and alcohols) containing one or more carbon atoms. Heterogeneous catalysts are known for producing alcohols. For example, U.S. Patent No. 3,326,956 describes a process for producing oxygenated hydrocarbons, especially methyl alcohol, which comprises contacting, at elevated temperatures and pressures, a mixture of hydrogen, carbon monoxide and carbon dioxide with a solid catalyst comprising the product of partly reducing the mixed oxides of copper, zinc and chromium.

U.S. Patent No. 4,122,110 discloses a process for manufacturing alcohols, particularly linear saturated primary alcohols, by the reaction of carbon monoxide (optionally with carbon dioxide being present also) and hydrogen in the presence of a catalyst containing four essential elements: copper, cobalt, a third metal selected from chromium, iron, vanadium and manganese, and a fourth metal which is an alkali metal ; and optionally zinc. U.S. Patent No. 4,291,126 discloses a related catalyst containing 20-60% copper, 5-50% cobalt, 5-30% of a metal selected from chromium, iron, vanadium and manganese, 5-40% of a rare earth metal, 0.1-5% of an alkali metal or alkaline earth metal and, optionally, zinc and/or a noble Group VIII metal and/or a binder.

U.S. Patent No. 4,199,520 discloses a rhodium catalyst which is useful for the manufacture of polyhydric alcohols, particularly ethylene glycol, from synthesis gas (i.e., a mixture of predominantly carbon monoxide and hydrogen) and which comprises a rhodium carbonyl sulfur cluster compound, the anion of which may be represented by

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the following empirical formula $[\text{Rh}_{17}(\text{S})_2(\text{CO})_{32}]^{-3}$ and the cation of which includes alkali metals.

U.S. Patent No. 4,377,643 discloses a catalytic process for converting synthesis gas to alcohols and alkanes comprising contacting carbon monoxide and hydrogen with a catalyst of the formula

$\text{A}_a \text{Ru}_b \text{Cu}_c \text{M}_d \text{N}_z \text{O}_x$
 wherein A is an alkali metal, M is Rh, Ir, Pd, Pt or mixtures thereof, a is about 0.002 to about 0.5, b is about 0.5 to about 3, c is about 0.5 to about 3, d is about 0.05 to about 0.5, z is a level of 0 to about 1 weight % and x is the number of oxygens needed to fulfill the valence requirements of the other elements.

U.S. Patent No. 4,235,798 discloses a process for selectively preparing a mixture of two-carbon atom oxygenated hydrocarbons (i.e., acetic acid, ethyl alcohol and acetaldehyde) by contacting hydrogen and carbon monoxide with a solid catalyst comprising rhodium in combination with one or more alkali metals under reaction conditions to favor the formation of such products.

U.S. Patent No. 4,235,801 discloses a process for producing ethyl alcohol from synthesis gas employing a catalyst essentially comprising rhodium and iron.

Molybdenum-based catalysts have also been used to catalyze a variety of reactions such as desulfurization, denitrofication and hydrogenation reactions. For example, U.S. Patent No. 2,490,488 discloses the use of a molybdenum sulfide catalyst promoted with "minor proportions" of an alkali metal oxide, hydroxide or carbonate to produce liquid hydrocarbons and organic oxygen-containing compounds from carbon monoxide and hydrogen. The preferred amount of the alkali promoter,

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according to the patent, is about 0.5 to 5 weight percent based on the weight of molybdenum sulfide, or 2-20 mole percent when the promoter is potassium hydroxide. Carbon monoxide and hydrogen are said to be converted to normally liquid hydrocarbons and unspecified organic oxygen-containing compounds utilizing such catalyst.

U.S. Patent No. 4,199,522 discloses a process for the production of C_2-C_4 olefinic hydrocarbons from synthesis gas using a catalyst consisting essentially of 1-95% by weight of at least one material selected from the group consisting of the sulfide, oxide and metal of molybdenum, tungsten, rhenium, ruthenium, nickel, palladium, rhodium, osmium, iridium and platinum, and 0.05-50% by weight of at least one material selected from the group consisting of the hydroxide, oxide or salt of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba and Th. U.S. Patent No. 4,151,190 discloses a similar catalyst. There is no disclosure in either patent that such a catalyst produces oxygenated products.

A number of prior art references disclose so-called oxo processes which include the hydrogenation of aldehydes to alcohols in the presence of supported and unsupported molybdenum sulfide catalysts at elevated temperatures and pressures. The starting aldehydes are produced in the first step of the oxo process by carbonylating an olefin by reaction with carbon monoxide and hydrogen. These references include French Patent No. 1,315,275 and U.S. Patent Nos. 2,709,714, 2,813,911, 2,976,254, and 3,118,954.

J.F. Shultz, et al., Bureau of Mines Report of Investigations, No. 6974, U.S. Dep't. of the Interior (1967) report that molybdenum oxide and sulfide, used as methanation catalysts, produce up to 20% of the products as two to four-carbon atom hydrocarbons. However, there

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is no disclosure in this article concerning alcohols or any other oxygenated products from such systems.

In addition to the foregoing, published prior art, the present inventor is aware of an unpublished study, by a colleague, of catalysis by molybdenum sulfide. During that study, he observed that alcohols may be produced from carbon monoxide and hydrogen using a molybdenum sulfide catalyst containing small amounts (i.e., up to about 0.30 mole of alkali per mole of molybdenum) of an alkali such as potassium hydroxide. One experimental run (at 250°C, 400 psig, a CO/H₂ molar ratio of 1/3, a GHSV of 3000 hr⁻¹ and a potassium loading of about 0.15-0.18 mole per mole of molybdenum) produced the following results:

Selectivities (%)

methyl alcohol = 46
ethyl alcohol = 26
n-propyl alcohol = 1
methane = 27

Rate of total alcohol production = 1.8
pounds per cubic foot of catalyst per hour

In another experimental run, under the same conditions and employing a molybdenum sulfide/KOH catalyst prepared to contain about 0.30 mole potassium per mole molybdenum, the following results were obtained:

Selectivities (%)

methyl alcohol = 35
ethyl alcohol = 19
n-propyl alcohol = 9
methane = 37

Rate of total alcohol production = 1.9
pounds/ft³ of catalyst/hour

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SUMMARY OF THE INVENTION

It has now been found that mixtures of alcohols may be produced at high selectivities and at high rates by reacting carbon monoxide and hydrogen over a heterogeneous catalyst consisting essentially of molybdenum sulfide and a significant amount of a compound of an alkali metal. In summary therefore, the process of the present invention comprises reacting carbon monoxide and hydrogen in the vapor phase, in the presence of a heterogeneous catalyst consisting essentially of molybdenum sulfide and an alkali metal compound at a gas hourly space velocity of at least about 3000 hr^{-1} , to selectively produce mixtures of linear, C_1 - C_5 alcohols at high rates. The alkali metal compound is present in the catalyst in an amount of at least about 0.20 mole per mole of molybdenum. Depending upon the amount of alkali metal compound in the catalyst, the reaction conditions of gas hourly space velocity, temperature and pressure may be varied to obtain the product alcohols at high selectivities and high rates.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention converts carbon monoxide and hydrogen primarily to mixtures of linear, primary alcohols (i.e., substantially all primary alcohols with no carbon branching), containing principally one to five carbon atoms. Produced as by-products may be some longer-chain alcohols (i.e. C_6 and higher alcohols), secondary and/or branched-chain alcohols, saturated and unsaturated hydrocarbons and small amounts of aldehydes, ketones and esters. Compared to known processes for preparing such linear alcohols, the process of the present invention offers some advantages. For example, the catalyst used in the present invention is a relatively

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simple, easily-prepared system. Another important advantage is the high alcohol yields obtained by the present invention. Most previously-known catalysts produce large quantities of hydrocarbons or hydrocarbons and very little alcohols. A further advantage of the process of the invention is the ability to favor the production of alcohols of longer or shorter chain lengths by careful regulation of reaction conditions. As will be seen from the following description, by suitable adjustments of certain reaction conditions (e.g., GHSV, pressure, temperatures, the particular alkali metal and alkali-loading) alcohols of different chain-lengths may be produced. While some of the prior art provides one or more of these advantages, only the present invention demonstrates all of these advantageous properties.

More specifically, the process of the present invention is useful for the selective production of mixtures of substantially linear alcohols having from 1 to 5 carbon atoms, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, and n-pentyl alcohol. The process also produces minor proportions of secondary and branched alcohols, such as isopropyl alcohol, isobutyl alcohol, sec-butyl alcohol and iso-pentyl alcohol. However, the process is most useful in the production of C_1 - C_5 , normal alcohols. In fact, it has been observed that substantially all of the alcohol products of the process of the invention are normal alcohols. Normally, a mixture of alcohols is produced but by using particular catalysts and by suitable adjustments in the reaction conditions, as described below, the production of particular higher or lower alcohols may be favored. For example, under conditions which favor the higher alcohols, it is expected that the C_5 alcohols would be produced along with C_4 (and lower) alcohols.

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It has also been found that when an olefin is fed to the reaction with the synthesis gas, the olefin is converted to an alcohol containing one more carbon atom than the starting olefin. This is the subject of a commonly-assigned, U.S. Patent application filed on even date herewith, in the name of the same inventor (Attorney Docket D-14,105, entitled "Catalytic Process for the Production of Alcohols from Carbon Monoxide, Hydrogen and Olefins").

It is desirable to control the reaction conditions to minimize formation of by-products. Typically, the most prevalent by-products are hydrocarbons (both saturated and unsaturated) although the present invention generally provides a highly selective route to alcohols over hydrocarbons. Preferably, hydrocarbon by-products are produced in amounts, relative to total alcohol production, of less than about 20 mole %. Specifically, higher gas hourly space velocities (GHSV) favor alcohol production over hydrocarbons. Other possible by-products may include small amounts of other oxygenated products such as C_6 and higher alcohols, secondary and/or branched-chain alcohols, and aldehydes, ketones and esters. Such oxygenated by-products are generally produced in amounts, relative to the total alcohol production, of less than about 10 mole %, optimally less than about 2-3 mole %.

The reaction of the present invention is conducted in the vapor phase by reacting carbon monoxide and hydrogen in the presence of the solid, heterogeneous molybdenum sulfide-alkali metal catalyst. The desired mixture of C_1 - C_5 , linear, primary alcohols may be separated and recovered from the gaseous reaction products and from each other by any suitable technique known to those skilled in the art. In addition, any conventional equipment may be employed in the process of the invention, with suitable

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regard for the reactants, conditions of reaction and products.

The carbon monoxide and hydrogen reactants may conveniently be derived from so-called synthesis gas which is primarily a mixture of carbon monoxide and hydrogen, although it may typically also contain a very small amount of sulfur compounds as well as small amounts of carbon dioxide, and nitrogen and other inert gases, depending on its source. Synthesis gas is produced commercially, for example, as a product of the partial combustion of coal, natural gas, petroleum bottoms or other carbonaceous materials. A specific method of synthesis gas derivation is the heating of coke in the presence of air and then steam. The molar ratio of carbon monoxide to hydrogen (CO:H_2) in synthesis gas may vary widely from about 1:10 to about 10:1; for purposes of the present invention, the preferred molar ratio CO:H_2 is from about 2:1 to about 1:4. Of course, rather than employ synthesis gas, which is the preferred reactant feed, it is also possible to use as a feed gas any gas containing predominantly carbon monoxide and hydrogen within the foregoing ratios. Regardless of the source of the carbon monoxide and hydrogen reactants, it is expected that the gas feed to the reaction may contain small amounts of sulfur compounds without deactivating substantially the molybdenum sulfide-alkali metal catalyst.

The catalyst consists essentially of molybdenum sulfide and a member selected from the group consisting of an alkali metal compound and mixtures thereof. The precise catalytic specie or species are not known with certainty. It is possible that operating temperatures, pressures, and catalyst preparation methods as well as the feed gases, may have an effect on the structure or activity of the catalyst. The precise effects are not readily

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ascertainable and are difficult to measure. For this reason, it is not possible to describe with reasonable certainty the structure of the active catalytic specie or species. However, it is known that when the molybdenum sulfide precursor of such catalysts is prepared by methods described hereinbelow, it exhibits an x-ray diffraction pattern characteristic of crystalline molybdenum disulfide. Since x-ray diffraction only characterizes bulk crystalline phases and it is very likely that the catalyst surface contains some oxygen in addition to molybdenum and sulfur, possibly as oxythiomolybdates, nevertheless, for ease of description, the molybdenum will be described herein sometimes as the sulfide. Subsequently, the alkali metal compound is added to that molybdenum sulfide to provide the highly selective catalyst of the invention. However, the form of the alkali metal in the active catalytic system may not be the same as the alkali metal compound that was introduced to the molybdenum sulfide. For purposes of the present invention, it is sufficient if the alkali metal compound is added as described herein, regardless of the particular form it may take in the active catalyst. The alkali metal compound may be added to the molybdenum sulfide by the so-called incipient wetness technique, known to those skilled in the art, and described hereinbelow, or by any other method known to those skilled in the art such as ion exchange or precipitation. The resulting catalyst is said to consist essentially of molybdenum sulfide and a member selected from the group consisting of an alkali metal compound and mixtures thereof.

The minimum amount of alkali metal compound in the catalyst must be that amount necessary to provide selectivity to alcohols rather than hydrocarbons and will vary depending upon the particular alkali metal compound and the reaction conditions. An amount as low as about

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0.20 mole of alkali metal compound per mole of molybdenum may be employed if certain preferred alkali metal compounds (e.g., potassium, rubidium or cesium compounds) are employed and/or if reaction conditions are selected which favor alcohol production over hydrocarbons (e.g., higher GHSV's, higher pressures and lower temperatures). The preferred lower limit of alkali metal in the catalyst is about 0.30 mole of alkali metal compound per mole of molybdenum. The upper limit of the amount of alkali metal compound in the catalyst is not absolutely fixed and amounts as high as about 2 moles per mole of molybdenum have been used with good results. Therefore, as a general rule, amounts of alkali metal compound of from about 0.30 to about 2 moles per mole of molybdenum may be employed in the present invention. It is preferred however that the catalyst contain from about 0.30 to about 0.70 mole of alkali metal compound per mole of molybdenum.

The catalyst may be prepared by conventional means, such as by adding an alkali metal compound to a sulfur-containing molybdenum compound such as MoS_3 , MoS_2 , ammonium oxythiomolybdate or ammonium polythiomolybdate (which compounds may be obtained commercially or prepared from a variety of molybdenum compounds) by, for example, impregnation with a solution of the alkali metal compound (i.e., an incipient wetness technique), co-precipitation, by grinding and calcining a dry alkali metal compound with the molybdenum compound or by ion exchange. Another method of preparing the catalyst comprises sulfiding a commercially-available alkali metal molybdate or a molybdenum oxide such as MoS_3 or MoO_2 , after treatment with an alkali compound. A preferred method of preparing the catalyst comprises decomposing a thiomolybdate salt to produce molybdenum sulfide (e.g., as described in U.S. Patent Nos. 4,243,553 and 4,243,554) and

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then adding the alkali metal compound by a suitable technique, such as the incipient wetness method. This method is preferred since it produces a catalyst more active for the production of linear, primary, $C_1 - C_5$ alcohols than catalysts prepared by the other enumerated techniques.

More specifically, in a preferred method, molybdenum sulfide may be prepared by decomposing a thiomolybdate salt, such as ammonium thiomolybdate ("ATM") or ammonium polythiomolybdate, at an elevated temperature (e.g., on the order of about 300-600°C) in a gaseous atmosphere such as nitrogen or hydrogen or mixtures thereof. Other gases may be employed, such as an inert gas, carbon monoxide, etc. The ammonium thiomolybdate or other salt may be prepared by known methods, such as (in the case of ammonium thiomolybdate) by bubbling hydrogen sulfide through an ammonium hydroxide solution of ammonium hepta molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, at elevated temperatures (e.g., about 30-40°C). The alkali metal compound may be added to the molybdenum sulfide by the so-called incipient wetness technique known to those skilled in the art. This technique generally comprises adding a pore volume of solution of the alkali metal compound to the dry molybdenum sulfide, under vacuum, followed by drying at elevated temperature under an inert gas such as nitrogen. If the amount of alkali metal compound that can be added to the molybdenum sulfide is less than desired because of limited solubility of the particular alkali metal compound employed, the procedure may be repeated until the desired alkali metal compound to molybdenum ratio is obtained.

The particular alkali metal compound contained in the catalyst of the invention does have an effect upon the alcohol selectivity of that catalyst. Generally, those

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compounds may be selected from inorganic and organic salts, hydroxides, oxides and sulfides of alkali metals and mixtures thereof. It is expected that all organic and inorganic salts of alkali metals will form catalysts which can give good selectivity to alcohols. Examples of suitable inorganic salts are the nitrates, sulfates, carbonates and chlorides of the alkali metals (e.g., sodium, potassium, lithium, cesium and rubidium); examples of suitable organic salts are the acetates, citrates, methoxides and ethoxides of the alkali metals. Specific examples of suitable alkali metal compounds useful in this invention include potassium hydroxide, potassium acetate, potassium nitrate, cesium chloride, cesium sulfate, cesium acetate, lithium nitrate, sodium nitrate, rubidium acetate, and the like. The hydroxides, acetates and sulfates are preferred. Among the various alkali metals, the potassium, cesium and rubidium compounds are preferred. Particularly preferred compounds are potassium hydroxide, potassium acetate, cesium acetate and cesium sulfate.

The solid catalyst may be employed in any convenient form depending upon the conditions of reaction and the equipment employed. For example, the catalyst, normally obtained as a powder by grinding or milling, may be made into other conventional forms such as pellets, tablets, granules, and the like by known methods, or may be supported on any suitable inert support. Similar results have been obtained with laboratory-scale fixed-bed reactor systems employing catalyst as a powder or as 20-40 mesh particles, although on a commercial scale, it probably would be desirable to use larger mesh. In the case of fluidized-bed operations, a powdered catalyst of suitable size may be appropriate. Those skilled in the art will be able to practice the invention by selecting the form and size of catalyst, based on the conditions encountered in

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use. If a supported catalyst is desired, any typical inert support may be employed, such as carbon, silica, alumina, titania, silica-alumina, silica-titania, magnesia, molecular sieves and zeolites, clays, and the like. The supported catalysts may be prepared by techniques analogous to those employed for the unsupported catalysts, such as an incipient wetness technique using ammonium hepta molybdate and potassium acetate in aqueous solution. Supported catalysts or pelletized or extruded unsupported catalysts are favored in large-scale, fixed-bed systems. Slurry systems are conveniently operated with finer catalyst particles. The use and selection of supported or unsupported catalyst systems to suit various reactor systems is readily understood by those skilled in the art.

To produce the desired mixtures of C_1 - C_5 , linear, primary alcohols, the carbon monoxide and hydrogen feed are reacted in the vapor phase in suitable equipment, in the presence of catalyst, under suitable conditions of gas hourly space velocity (GHSV), temperature and pressure. The reaction can be directed to higher or lower product alcohols by suitable control of the alkali content of the catalyst and the reaction conditions.

The GHSV of the feed gas is defined as the volume of gas fed per volume of catalyst charge per hour (expressed as reciprocal hours, hr^{-1}) and it has been unexpectedly found that high GHSV's result in high selectivities to the desired alcohols. For purposes of the present invention, the GHSV should be at least about $3000\ hr^{-1}$, preferably at least about $6000\ hr^{-1}$, most preferably at least about $12,000\ hr^{-1}$. With lower GHSV's, hydrocarbon selectivity increases at the expense of alcohol selectivity. There is

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no known maximum GHSV and it will depend in part on the economics of the equipment used. With GHSV's much higher than 12000 hr^{-1} , alcohol selectivity is not substantially changed and while the rate of alcohol production does increase with higher GHSV's the total conversion to product decreases slightly.

The temperature at which the process of the invention may be performed is not particularly critical and may be varied depending on the results desired. As a general rule, the temperature of the process may be from about 250°C to about 400°C , and a temperature of from about 275°C to about 350°C is preferred. As can be seen from the examples which follow, use of higher process temperatures tends to favor production of longer-chain alcohols over shorter-chain alcohols. However, when higher temperatures are used, a larger proportion of hydrocarbons is also produced. Therefore, depending on the particular catalyst, the reaction conditions may be varied to obtain the desired results.

The pressure of the reaction is not critical and may be from about atmospheric to about 2,000 psig, depending on the equipment used and results desired. Generally, increasing pressure tends to favor alcohols over hydrocarbons but also favors shorter-chain products (both alcohols and hydrocarbons) over longer-chain products.

The product $\text{C}_1\text{-C}_5$ alcohols have many and varied industrial uses. For example, they are useful as solvents and also as intermediates for the production of, for example, plasticizers for synthetic resins or as fuel additives.

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The examples which follow are meant to further illustrate the present invention (except for the comparative examples) and are presented to enable those skilled in the art to practice the present invention. They are not intended to limit the invention. Rather, it is intended that the invention be limited only by the scope of the claims appended hereto.

Except as noted in the examples (all of which describe work actually performed), the molybdenum sulfide catalyst was prepared by decomposing ammonium thiomolybdate (ATM) at an elevated temperature, usually 400°C, in nitrogen containing 10 volume percent hydrogen. The ammonium thiomolybdate was prepared by bubbling hydrogen sulfide through an ammonium hydroxide solution of ammonium hepta molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, at 30-40°C. The molybdenum sulfide prepared in this manner exhibited an x-ray diffraction pattern typical of molybdenum disulfide and surface areas of 10-60 square meters/gram. The alkali metal compound additive was then introduced into the molybdenum sulfide by an incipient wetness technique. Specifically, the molybdenum sulfide was first evacuated for 1 hour using a rotary vacuum pump and then an aqueous solution of the alkali metal compound was introduced onto the molybdenum sulfide with a syringe. The volume of the solution added was equivalent to one pore volume of the molybdenum sulfide, i.e., the volume required to fill the void volume of the molybdenum sulfide. If excess liquid was added, the catalyst was allowed to dry under a vacuum until no liquid was present. The resulting wet material was dried under a flow of nitrogen at 85°C for 1 hour and then 110°C for 2 hours. It was then ground to a uniform powder and added to a tube at 400°C under a flow of 20 parts by volume of hydrogen and 180 parts by volume of nitrogen. After one

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hour at 400°C, the hydrogen flow was stopped and the material cooled to ambient temperature.

The supported catalysts employed in the examples were also prepared by the incipient wetness technique using ammonium hepta molybdate and potassium acetate in an aqueous solution. The inert supports were washed with oxalic acid before use to remove impurities by passing a mixture of oxalic acid, glycerine, and water in proportions of 1:1.5:2.5 by weight, respectively, through a bed of support material (length/diameter ratio of about 20 to 25) contained within a glass tube which drained through a stopcock at its base. The contents of the tube were maintained at about 90°C by means of resistance heating wire wrapped around the exterior of the tube. About 2.5 volumes of oxalic acid solution were used to wash one volume of 8-20 mesh support material over a three-hour period. The material was then washed with about six volumes of distilled water at 90°C over a period of about four hours and then dried at 350°C for about four hours.

The reactor used in the examples was a continuous feed, U-shaped, stainless steel, tubular reactor with no recycle. Gas samples were routinely analyzed by conventional gas chromatographic techniques. Product identifications were initially confirmed by the use of a mass spectrometer. The catalyst was loaded into the stainless steel U-tube with 0.5 mm quartz beads above and below the catalyst bed. If an unsupported catalyst was used, it was prepared as powder and then mixed with an equal volume of 0.5 mm quartz beads. Supported catalysts were loaded as 20-40 mesh particles. Once installed, the reactor was pressure tested and then flushed several times with nitrogen before the reactant gas mixture (carbon monoxide and hydrogen) flow was started. After the

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desired flow and pressure were established, the reactor was heated to reaction temperature in a fluidized sand bath. A gas sample was analyzed one hour after the fluidized sand bath reached the reaction temperature and every hour thereafter until the end of the run.

Modifications to the reaction conditions were made immediately after a gas sample was injected into the chromatograph and the first sample at the new conditions was analyzed one hour later. The reactor was cooled to room temperature after each run with a slow flow of nitrogen passing through the catalyst. The data in the examples represents an average of several analyses.

Conversion was determined as the percent of carbon monoxide fed to the reactor converted to product; and selectivity to a particular product is stated as the number of moles of carbon in that particular product as a percentage of the total number of moles of carbon in all products. A product is defined as any compound which is derived from synthesis gas other than CO_2 or H_2O .

Examples 1-3 and Comparative Example 1

A catalyst containing 0.2 mole of potassium hydroxide, per mole of molybdenum was prepared and charged into a tubular reactor, both as described above. Several runs, including a comparative example, were made at 300°C and at different pressures and gas hourly space velocities GHSV (defined as liters of carbon monoxide and hydrogen gas fed per liter of catalyst charge per hour). The results are shown in Table I below. Based on the data in Table I, it is apparent that increasing the space velocity causes a shift in product distribution from hydrocarbons to oxygenated products. It is also apparent that an increase in the pressure further increases the selectivity to oxygenated products.

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TABLE I

<u>Example</u>	<u>GHSV (hr⁻¹)</u>	<u>Pressure (psig)</u>	<u>Conversion (%)</u>	<u>Selectivity (%)</u>	
				<u>Hydrocarbons</u>	<u>Oxygenated Products*</u>
Comp. Ex. 1	300	200	14	95	5
1	3000	200	7.3	79	21
2	3000	400	10.8	63.5	36.5
3	12000	400	6.5	51.1	48.9

* Including alcohols, esters and aldehydes

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Examples 4-8 and Comparative Examples 2-4

A series of catalysts were prepared by the method described above, all containing 0.616 mole of different alkali metal or alkaline earth metal compounds per mole of molybdenum. These catalysts were charged to a tubular reactor as described above and carbon monoxide and hydrogen were reacted under the following reaction conditions:

temperature (°C)	300
pressure (psig):	400
GHSV (hr ⁻¹):	12,000
H ₂ /CO (molar):	1

The results are shown in Table II below.

TABLE II

Example	alkali compound	Conversion (%)	Selectivity (%)				Alcohol Rate (lb./CF/hr.)
			MeOH	EtOH	PrOH	BuOH	
4	lithium nitrate	0.9	13	8	3	0	0.8
5	sodium nitrate	1.2	29	15	7	2	1.2
6	potassium nitrate	2.0	30	13	10	2	2.3 - 5.3
7	rubidium acetate	2.3	36	23	6	1	6.3
8	cesium acetate	4.8	47	27	5	1	16.0
Comparative Examples							
2	magnesium acetate	3.1	--	--	--	--	--
3	calcium acetate	0.8	5	1	--	--	1
4	barium hydroxide	0.4	26	11	4	--	0.7

Notes:

MeOH = Methyl alcohol

EtOH = Ethanol

PrOH = Total Propanol

BuOH = Total Butanol

H.C. = Total Hydrocarbons

lb./CF/hr. = Total pounds of alcohols produced per cubic foot of catalyst per hour

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Examples 9-15

Example 6 was repeated except that the anion of the potassium compound and total potassium in the catalyst system were varied. The results are shown in Table III below. The symbols have the same meaning as those used in Table II.

TABLE III

Example	Anion	Molar Ratio of Potassium to Molybdenum	Conversion (%)	Selectivity (%)				Alcohol Rate (lb./CF/hr.)
				MeOH	EtOH	PrOH	BuOH	H.C.
9	hydroxide	0.20	6.5	16.8	16.8	12.4	2.3	51.
10	hydroxide	0.60	4.4	35.5	36.6	5.6	0.6	19
11	acetate	0.60	1.7	39.5	29.7	8.0	2.2	17.9
12	acetate	2.20	2.6	43.6	27.2	8.7	0.8	14.9
13	nitrate	0.33	2.9	22.9	14.6	4.6	0.7	44
14	nitrate	0.60	2	30	13	20	2.0	28.
15	nitrate	1.00	1.3	45.4	26.1	6.9	-	18.9

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Example 16-19

These examples illustrate the wide variety of anions which may be used as part of the alkali metal compound which forms a part of the catalyst used in the process of the present invention. Examples 16 and 17 illustrate the use of potassium tartrate, while examples 18 and 19 show the use of potassium citrate. Both of these compounds give good rates and selectivities, but the citrates are preferred.

These examples also serve to demonstrate the effect of higher gas hourly space velocities in the process of the present invention. From these examples, it can be seen that an increase in the gas hourly space velocity from $12,000 \text{ hr}^{-1}$ to $24,000 \text{ hr}^{-1}$ causes a slight decrease in total conversion but significantly increases the alcohol production rate and the selectivity towards alcohols.

The reaction conditions and results of these examples are set forth in Table IV below.

TABLE IV

Example	Anion	Molar Ratio of Potassium to Molybdenum	Conversion (%)	Selectivity (%)				Alcohol Rate (lb./CF/hr.)
				MeOH	EtOH	PrOH	BuOH	
16	Tartrate(a)	0.6	1.4	50.0	30.8	3.1	N.D.	15.2
17	Tartrate(b)	0.6	1.3	58.4	28.8	5.2	0.6	6.4
18	Citrate(c)	0.6	2.0	42.9	31.6	3.3	0.1	20.7
19	Citrate (d)	0.6	1.7	54.5	30.4	6.1	0.7	7.7
								14.0

- a Reaction conditions: 300°C, 400 psig, H₂:CO = 1:1, GHSV = 12,000 hr⁻¹
- b Reaction conditions: 300°C, 400 psig, H₂:CO = 1:1, GHSV = 24,000 hr⁻¹
- c Reaction conditions: 300°C, 400 psig, H₂:CO = 1:1, GHSV = 12,000 hr⁻¹
- d Reaction conditions: 300°C, 400 psig, H₂:CO = 1:1, GHSV = 24,000 hr⁻¹

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Examples 20-23

The use of various cesium compounds is demonstrated in Examples 20-23. In these examples the anion of the cesium compound and the mole ratio of cesium compound to molybdenum was varied. The catalyst system was charged to the reactor and the reaction was conducted at a pressure of 400 psig, a temperature of 300°C, a GHSV of 12,000 hr^{-1} and a CO/H_2 molar ratio of 1.0. The results are set forth in Table V below. The symbols are the same as in Table II.

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Examples 24-31

The molybdenum sulfide used in Examples 1-15 and 20-23 above was pretreated at 400°C in a mixture of 10 parts by volume of hydrogen and 90 parts by volume of nitrogen. When the pretreatment temperature was raised, the selectivity tends to shift toward the higher alcohols. The following Table VI shows the results obtained using a catalyst system containing 0.616 mole of potassium acetate per mole of molybdenum at various molybdenum sulfide pretreatment temperatures, in a mixture of 10 parts of hydrogen and 90 parts of nitrogen. The other reaction conditions were: GHSV = 12,000 hr⁻¹; H₂/CO (molar) = 1.0; pressure = 400 psig. The symbols are the same as in Table II

TABLE VI

Example	Pre-treatment Temp. (°C)	Reaction Temp. (°C)	Conversion (%)	Selectivity (%)					Alcohol Rate (lb./CF/hr.)
				MeOH	EtOH	PrOH	BuOH	H.C.	
24	400	300	1.7	39.5	29.7	8.0	2.2	16.3	5.6
25	400	300	2.1	44.0	47.0	8.0	1.0	15.0	7.1
26	400	350	3.4	25.0	47.0	23.0	6.0	25.0	8.2
27	400	350	3.8	15.4	23.9	11.6	2.9	41.7	7.7
28	500	300	3.0	23.8	42.5	14.1	3.4	16.0	9.0
29	500	344	5.1	12.4	32.3	18.5	4.2	17.6	11.3
30	600	300	0.7	26.9	38.2	12.5	3.3	14.8	2.1
31	600	340	1.7	20.0	41.0	27.0	11.0	26.0	3.5

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Example 32-37

A catalyst system of 0.85-0.90 mole of cesium acetate per mole of molybdenum, was prepared and charged into the reactor as described above. Several runs were made at a pressure of 400 psig, a GHSV of $12,000 \text{ hr}^{-1}$ and a H_2/CO molar ratio of 1.0. The temperature was varied to demonstrate the effect of temperature on alcohol production. Similar runs were made under the same conditions using a catalyst of molybdenum sulfide and 0.85-0.90 mole of potassium acetate per mole of molybdenum. The data are summarized in Table VII and show that higher operating temperatures favor the production of longer chain alcohols. The symbols mean the same as those used in Table II.

TABLE VII

Example	Alkali Metal	Reaction Temp (°C)	Selectivity *		Selectivity **				Alcohol Rate (lb/CF/hr)
			(%)		(%)				
			H.C.	Total Alcohol	MeOH	EtOH	PrOH	BuOH	
32	Cs	250	7	90	86	11	2	1	3.7
33	Cs	300	18	80	59	34	6	1	16.0
34	Cs	350	28	66	34	29	29	8	9.0
35	K	300	15	81	55	33	11	1	9.0
36	K	325	20	73	38	36	22	4	9.7
37	K	350	33	65	25	34	32	9	10.9

* of total converted product

** of total alcohol products

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Example 38-42

Catalysts may be prepared by several methods other than the incipient wetness technique using molybdenum sulfide prepared from ATM, such as by sulfiding potassium molybdate in situ, impregnating commercially-available molybdenum disulfide, and intimately mixing dry potassium acetate and molybdenum sulfide. The results obtained when such catalysts are used in the process of the present invention are shown in Table VIII. Example 38 shows results obtained using a commercially-available potassium molybdate sample sulfided in situ with hydrogen disulfide at 400°C. The material contained a potassium:molybdenum molar ratio of 0.82. This catalyst did result in good selectivity to alcohols but at a lower rate than the other catalysts discussed. Examples 39 and 40 show the results for catalysts prepared by the incipient wetness technique using potassium acetate and commercially-available molybdenum disulfide with molar ratios of potassium to molybdenum of 0.60 and 2.00, respectively. These resulted in reasonable selectivity to alcohols but lower activity. Examples 41 and 42 are the results for catalysts prepared by grinding together dry potassium acetate and molybdenum sulfide prepared by the decomposition of ATM and then calcining at 400°C in a mixture of 10 parts by volume hydrogen and 90 parts by volume of nitrogen. The catalyst used in Example 44 contained a potassium:molybdenum molar ratio of 0.60 and exhibited a moderate rate of alcohols formation. Example 42 utilized a catalyst that contained a potassium:molybdenum molar ratio of 2.00 and shows a more desirable ratio of alcohol to hydrocarbon production distribution while retaining reasonable alcohol productivity. The symbols are the same as in Table II.

TABLE VIII

Example	Conv %	Selectivity (%)				Alcohol rate (lb./CF/hr.)
		MeOH	EtOH	PrOH	BuOH	H.C.
38	1.1	52.5	25.7	6.6	0.5	13.0
						1.04
39	0.15	37.9	25.2	9.1	-	22.1
						0.44
40	0.12	42.8	21.5	9.3	-	24.7
						0.35
41	2.43	20.0	10.9	5.7	2.5	54.0
						3.69
42	0.87	46.6	24.0	7.3	1.6	19.0
						2.89

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Examples 43-47

The use of optional supports for the catalysts employed in the process of the present invention is illustrated in Examples 43-47. A synthesis gas mixture was contacted with various supported catalysts at a temperature of 300°C, a pressure of 400 psig and a GHSV of 12,000 hr⁻¹. The supports used, the amount of support used and the resultant alcohol production are set forth in Table IX below. This data shows that the use of a magnesium oxide support will more strongly favor the production of shorter-chain alcohols than will the use of alumina or silica as supports. The symbols are the same as in Table II.

TABLE IX

Example	Support	Catalyst ^a Composition		Conv %	Selectivity (%)				Alcohol Rate (lb./GF/hr.)	
		wt%	wt%		MeOH	EtOH	PrOH	BuOH		
		Mo	K		H.C.					
43	Alumina ^a	24	3.6	0.69	9.8	31.0	18.4	3.0	31.6	1.57
44	Alumina ^b	24	1.9	0.43	42.7	31.8	4.5	-	19.9	1.44
45	Alumina ^b	24	3.6	0.25	62.0	16.03	-	-	18.5	0.92
46	Silica ^c	24	3.6	0.64	12.9	36.4	16.0	-	32.5	1.6
47	MgO ^d	24	3.6	0.72	60.4	20.3	12.7	0.8	4.5	1.74

^a alumina ("SA6173") obtained from the Norton Co. and washed with oxalic acid

^b alumina ("SA5534") obtained from the Norton Co. and washed with oxalic acid

^c silica ("59") obtained from the Davison Co. and washed with oxalic acid

^d magnesium oxide ("5500") produced by the Norton Co.

^e weight percentages are based on the weight of the entire catalyst including support

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WHAT IS CLAIMED IS:

1. A process for the selective production of mixtures of linear primary alcohols having 1 to 5 carbon atoms comprising reacting hydrogen and carbon monoxide in the vapor phase in the presence of a catalyst consisting essentially of molybdenum sulfide and at least about 0.20 mole, per mole of molybdenum, of a member selected from the group consisting of an alkali metal compound and mixtures thereof, wherein said hydrogen and carbon monoxide gas reactants are fed to said reaction at a rate of at least about 3,000 liters of gas per liter of catalyst per hour.
2. The process of Claim 1 wherein said alkali metal compound is selected from the group consisting of organic and inorganic salts, oxides, sulfides and hydroxides of alkali metals.
3. The process of Claim 1 wherein said alkali metal compound is a nitrate, sulfate or carbonate of an alkali metal.
4. The process of Claim 1 wherein said alkali metal compound is an acetate, citrate, tartrate, methoxide or ethoxide of an alkali metal.
5. The process of Claim 1 wherein said alkali metal compound is a compound of cesium, rubidium or potassium.
6. The process of Claim 1 wherein the molar ratio CO:H_2 is from about 1:2 to about 4:1.
7. The process of Claim 1 wherein the temperature of reaction is from about 250°C to about 400°C.

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8. The process of Claim 1 wherein said alkali metal compound is present in said catalyst in an amount of from about 0.30 mole to about 2 moles of alkali metal compound per mole of molybdenum.

9. The process of Claim 1 wherein said molybdenum sulfide is obtained by heating ammonium thiomolybdate at elevated temperatures.

10. The process of Claim 9 wherein said heating is at a temperature of about 300-600°C.

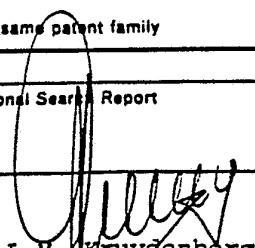
11. The process of Claim 1 where said alkali metal compound is a hydroxide of an alkali metal.

12. The process of Claim 1 where said alkali metal compound is an acetate of an alkali metal.

13. A process for the selective production of mixtures of linear, primary alcohols having 1 to 5 carbon atoms comprising reacting hydrogen and carbon monoxide in the vapor phase in the presence of a solid catalyst consisting essentially of molybdenum sulfide and from about 0.30 to about 0.70 mole per mole of molybdenum, of a member selected from the group consisting of an alkali metal compound selected from the group consisting of organic and inorganic salts, oxides, sulfides and hydroxides of alkali metals and mixtures thereof, at a gas hourly space velocity of at least about 6,000 hr⁻¹.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 84/02111

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 07 C 29/15; 31/04; 31/08; 31/10; 31/12		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 07 C 29/00; C 07 C 31/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB, A, 469959 (G.W. JOHNSON) 2 September 1937 see page 3, lines 35-66 --	1
A	US, A, 1741307 (A.O. JAEGER) 31 December 1929 see page 1, lines 48-94 -----	1
* Special categories of cited documents: ¹⁶ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
26th March 1985		02 MAY 1985
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		 G.L.M. Kruidenberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/US 8402111 (SA 8646)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 19/04/85

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 469959		None	
US-A- 1741307		None	

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