CATALYST AND METHOD FOR SYNTHESIS OF DIMETHYL ETHER

This invention relates to a method for converting synthesis gas (H_2 and CO) into dimethyl ether, and to a catalyst composition for use in that conversion.

There are at present two major routes for effecting the conversion of coal via synthesis gas into liquid fuels comprising the well publicized Fischer-Tropsch process and a more recently developed methanol to gasoline process such as that provided in U.S. Patent 3,928,483. The Fischer-Tropsch process produces a wide range of C_1 to C_{50} products comprising gases, liquid hydrocarbons, oxygenates and water.

Common to each of the above processes is the overriding influence of the capital cost of producing synthesis gas (syngas, H_2+CO). This varies with gasifier design, which is in turn influenced by coal properties and product enthalpy. A recent review of gasifier technology has identified some high efficiency gasifiers which of necessity produce synthesis gas having relatively low H_2/CO ratios resulting from utilizing low ratios of steam and oxygen in the gasification operation. Thus, the most recent advanced gasifiers operate at temperatures requiring relatively low product recovery temperatures and low steam to carbon ratios which translate into high thermal efficiency. The syngas produced under these conditions may have a H_2/CO ratio of 1 and more usually, for the highest efficiency gasifiers, of less than 1 and within the range of 0.4 to 0.7. Such low ratio syngas cannot be used directly in present day conventional Fischer-Tropsch processes and methanol syntheses, both of which require a H_2/CO ratio of or greater than 2. Thus, any external water-gas-shift operation to increase a H_2/CO ratio of 1 or less up to 2 or more would substantially cancel any gains in efficiency achieved by the most advanced high efficiency gasifiers.

A principal advantage to be gained in producing dimethyl ether (DME) directly from syngas is that it has been found that this

compound can be readily converted into gasoline boiling range hydrocarbons using a class of crystalline porotectosilicates, represented by ZSM-5 crystalline zeolite, for example as discussed in U.S. Patent 3,928,483, wherein the formed methanol is dehydrated and the ether product is converted over ZSM-5 crystalline zeolite.

Two publications dealing with synthesizing DME directly are British Patent 278,353 (1926) and German Offenlegungsschrift 2362944 (1974). The British patent claims a process for producing DME by contacting synthesis gas (H_2+CO) with a hydrogenating catalyst and a dehydrating catalyst at elevated temperatures and pressures, DME synthesis being obtained in the absence of the known shift reaction. In the German publication, the catalyst comprised a methanol synthesis component and a dehydrating component; in one example, a gas with H_2/CO ratio of 0.86 was contacted with a catalyst comprising Cu/Zn/Cr, in an atomic ratio of 82/16/4 and supported on alumina, at 250°C and 9800 kPa to achieve a syngas conversion of 77%, into a product containing 24.2% DME, 0.91% methanol, 27.3% CO_2, 0.41% H_2, 0.54% CH_4, and a balance of H_2, CO and N_2.

In more recent work, Sherwin and Blum reported in an Interim Report for May 1978 under the title "Liquid Phase Methanol", prepared for Electric Power Research Institute, Palo Alto, California, the attempt to produce DME by adding gamma- alumina and 13X molecular sieve to a slurry reaction system containing a commercial methanol synthesis catalyst. At 230-300°C, 3550-7000 kPa and 2015-6915 GHSV, only traces of DME were observed. A catalyst comprising Cu/Zn/Cr in an atomic ratio of 6/3/1 impregnated on Davidson 980 SiO_2/Al_2O_3, produced trace amounts of DME at 230°C, 7000 kPa and 2000 GHSV. The feed charged in the above experiments contained 50% H_2, 25% CO, 10% CO_2 and 15% CH_4.

It having been established that the direct conversion of syngas into DME is technically feasible, and it being known that the conversion of DME into gasoline boiling range hydrocarbons comprising olefins and aromatics can be achieved, the problem

remained of improving the conversion of syngas into DME to an economically attractive procedure.

In accordance with the present invention, there are now provided a catalyst composition and a process for the conversion of syngas into DME, the catalyst having reduced aging characteristics and being regenerable by oxidative techniques to maintain its high level of activity sufficient to sustain near equilibrium conversion of syngas into DME.

The present invention therefore provides a catalyst composition comprising co-precipitated Cu, Zn and Al components in amounts such that the atomic ratio Al/(Cu+Zn) is not less than 0.1 and the atomic ratio Cu/Zn is from 0.2 to 5.0, and an acidic dehydrating component.

The present invention also provides a method for converting syngas into an ether product which comprises contacting syngas having a H_2/CO ratio of 0.4 to 3, and water in an amount sufficient to compensate for any hydrogen deficiency in the syngas, with a catalyst composition as described above, at a temperature of 250 to 400°C, and recovering an ether product in an amount equivalent to at least 10% of the thermodynamic equilibrium conversion of the syngas.

The syngas conversion of the invention uses the metal components of a methanol synthesis catalyst in combination with an acidic dehydrating component. The catalyst compositions of the present invention rely upon the technique of co-precipitation of the hydrogenating components, either alone or mixed with the dehydrating component, the atomic ratio of the hydrogenating components Cu, Zn and Al being variable within the relatively narrow limits specified above. More particularly, co-precipitated components of Cu, Zn and Al are used in such relative amounts that the ratio Al/(Cu+Zn) is at least 0.1 and preferably from 0.1 to 2. A ratio of 0.2 to 0.7 is more particularly preferred. At the same time, the ratio Cu/Zn is from 0.2 to 5.0.

The acidic dehydrating component of the catalyst composition may be gamma-alumina, silica-alumina, a ZSM-5 type crystalline zeolite of high SiO_2 content, a phosphate, titanium oxide in combination with silicon oxide, a rare earth or a clay. Of these materials, gamma-alumina is particularly preferred, especially in an amount comprising about 50% of the catalyst composition.

The dimethyl ether synthesis techniques of this invention are of special interest since the ratio H_2/CO of the syngas feed may be less than 1 or greater than 1. Thus, the ratio H_2/CO may be from 0.4 to 3. However, it is particularly preferred to employ gas ratios equal to or less than 1, since such gas ratios are much more economically produced by modern high efficiency gasifiers and such a source of syngas can result in from 30% to 40% overall reduction in processing costs. In this low ratio syngas operating environment, it has been determined that the hydrogen deficiency of the low ratio syngas (H_2/CO of 0.4 to 0.7), can be remedied or compensated by injecting steam into the catalyst mass separately or in admixture with the low ratio syngas. This added steam is subject to a water-gas-shift reaction by the catalyst composition, resulting in a very effective and increased H_2/CO ratio gas in the catalyst reaction zone. This particular procedure eliminates the need for external water-gas-shift requirements to modify the low ratio syngas, thereby further contributing to the overall economic improvement of the process.

The investigations carried out in developing the present invention for obtaining direct conversion of syngas into dimethyl ether, and the concepts developed therefrom, have illustrated dramatically that certain selected catalyst compositions consisting of co-precipitated mixed oxides of Cu, Zn and Al mixed with a suitable acid component such as gamma-alumina, provide high catalyst activity and selectivity for effecting dimethyl ether synthesis. More importantly, however, was the finding that these catalyst compositions could be periodically oxidatively regenerated to maintain the desired high catalyst activity, that is, the particular

catalyst compositions of the invention can be maintained at high steady state activity for an extended period by relying upon particular oxidative regeneration and pretreatment techniques of relatively short duration. For example, the catalyst in the syngas reaction zone may be regenerated therein or it may be passed through a separate catalyst regeneration zone and then returned to the reaction zone to maintain desired catalyst activity and selectivity. The regeneration of the catalyst may be accomplished in a continuous, semi-continuous or an interrupted, for example periodic, manner depending upon whether a fixed bed or a moving catalyst system is employed.

The syngas conversion process of the invention is carried out by contacting the syngas having a H_2/CO ratio of 0.4 to 3 with the catalyst composition at a temperature of 250 to 400°C and preferably at a pressure of 5000 to 15,000 kPa. If necessary, a quantity of water may be mixed with the syngas feed or otherwise fed to the catalyst to supplement the hydrogen deficiency of the mixture by the water-gas-shift activity of the catalyst. An ether product, comprising a near equilibrium quantity of DME, is subsequently recovered by conventional means. The ether product of the process is equivalent to at least 10% of thermodynamic equilibrium conversion of the syngas, although it is generally possible to adjust operating conditions to achieve at least 50% of thermodynamic equilibrium conversion.

The methanol synthesis/water-gas-shift component of the catalyst compositions of the invention comprises Cu/Zn/Al prepared by coprecipitation of copper, zinc and aluminum from a common solution. A preferred method of preparation of this catalyst component comprises dissolving nitrate salts of the metal components, in the desired molar ratios and concentrations, in an aqueous solvent and subsequently adding excess sodium carbonate thereto and precipitating the metal carbonates. The mixed precipitate is then recovered, washed to remove soluble nitrates and carbonates, dried and calcined. Of course, other soluble salts of

the metal components may be utilized in place of the nitrate salts and the precipitate may take the form of something other than the carbonate. Also, solvents other than water may be employed. The important factor, however, is that the metal components first be mixed in the desired molar ratios, in solution, and then co-precipitated to form a solid containing those components. The subsequent calcination step will oxidize the metals to their respective oxides.

The dehydrating component of the catalyst is preferably an acidic component selected from materials such as gamma-alumina, porotectosilicates including clays and natural or synthetic crystalline aluminosilicates, and zeolites. Especially preferred are gamma-alumina and crystalline zeolites having a Constraint Index within the approximate range of 1-12 and a high silica content. Other useful dehydrating components include phosphates, titanium oxide in combination with silicon oxide, rare earths and clays.

The methanol synthesis and dehydration components of the catalyst are combined by physical mixing of powders of the two components, either dry or in a slurry, followed by pelleting or extrusion, as appropriate. An inert or acidic binder may be included in the mixture to improve pellet/extrudate physical properties. Approximately 5 to 95 wt.% of the catalyst composition should comprise the dehydration component, although it is preferred to utilize from 20% to 70% dehydration component, based on the weight of the catalyst composition, excluding any binder therein.

As stated above, an especially desirable characteristic of the catalysts of the present invention, which contain both methanol synthesis/water-gas-shift and acid dehydration components, is that they are oxidatively regenerable, thereby prolonging their useful lives well beyond that of other, non-regenerable, catalysts. Regeneration may be accomplished periodically or continuously, depending on whether a fixed or moving catalyst system is employed. The basic technique for regenerating a spent catalyst is to pass an oxygen-containing gas over the catalyst while heating to an elevated

temperature of 250 to 540°C, it being preferred to employ temperatures below about 540°C for any extended operating period. The regeneration may be continued for a relatively short time or until there is a breakthrough of the oxygen-containing regenerating gas.

Following oxidation or regeneration of the catalyst, it has been found to be important, if not essential, to avoid contacting the freshly oxidized catalyst with a high-temperature reducing gas, for example H_2. That is, reducing the freshly regenerated catalyst with hydrogen or any other hydrogen-rich reducing gas should be avoided, particularly where the contact temperature equals or exceeds 260°C. It is preferred, therefore, to contact the oxygen regenerated catalyst with a reducing gas such as a syngas feed or a diluted syngas at a temperature which, initially, is from 175 to about 235°C and thereafter to raise the temperature and/or change the composition of the syngas feed to achieve near thermodynamic yields of DME.

As mentioned above, dimethyl ether synthesis offers decided advantages over other Fischer-Tropsch and methanol syntheses since it particularly lends itself to utilizing a syngas relatively low H_2/CO ratio, for example of $H_2/CO = 1$, with high selectivity to products convertable to liquid fuels or chemicals. This particular operation can be used to advantage in combination with any of the new high efficiency gasifying operations producing low ratio syngas by the injection or addition of water (steam) with the low ratio syngas feed passed into contact with the catalyst of the invention and suitable for DME synthesis. In this operation, the water-gas-shift capability of the catalyst is used to advantage. The DME produced may subsequently be converted into gasoline boiling range hydrocarbons by contact with ZSM-5 or similar crystalline zeolite material by methods described in numerous publications.

The direct synthesis of dimethyl ether from syngas can be utilized with considerable advantage in many different combination operations. That is, the economic formation of dimethyl ether using

a low ratio syngas and obtained from an efficient syngas generation operation or obtained, for example, by in situ gasification of coal, is particularly instrumental in providing competitive routes for producing specific chemicals and/or hydrocarbons varying considerably in composition.

The DME product obtained by the cofeeding of water with low ratio syngas has a principal effect of increasing syngas utilization by means of the shift reaction with excess CO to form additional hydrogen. An additional result of the cofed water operation is to increase the ratio of H_2/CO recovered in the effluent of the syngas conversion operation up to at least a H_2/CO ratio of 1.

The DME product of the synthesis of the present invention may be upgraded to t-butyl methyl ether (TBME) by reaction with a suitable alcohol, such as t-butanol, or with branched olefins such as 2-methylpropene, by utilizing an acid catalyst. The acid catalyst may be sulfuric acid or another mineral acid, with or without a support material. An acidic ion exchange resin may also be used as the acid catalyst. Phosphoric acid on a support material may also be used. The operating temperature may be from 50 to 300°C, with a temperature of 60 to 150°C being particularly preferred. A pressure in the range of 300 to 5000 kPa is suitable for the operation.

Alternatively, the syngas initially obtained from a gasification operation can be converted to a product rich in dimethyl ether in a catalyst slurry reaction system, in which the metal and acid components of the catalyst are surrounded with or suspended in a high boiling liquid phase. Liquids for such a system include minerals oils, oil products of Fischer-Tropsch synthesis such as a portion of the decant oil product, and lubricating oil base stocks. The solid catalyst components may be used as combined particles or as separate particles of the metal and acidic components. In this liquid phase operation, the temperature will generally be from 260 to 343°C and the pressure will generally be from about 7000 to 14,000 kPa.

Further, the DME product may be converted to methanol by reacting it with water in the presence of an acid catalyst. The catalyst may be phosphorus pentoxide distributed on kieselguhr, silica-alumina, alumina, reduced tungsten oxide or an acid crystalline zeolite. A temperature of from about 205 to about 370°C, and a pressure of from 1000 to 10,000 kPa will generally be used.

Still further, the DME product may be reacted with oxygen in the presence of a copper catalyst to form formaldehyde. In such an operation, the temperature may be from about 600 to 720°C and the pressure from 100 to 500 kPa. It is also possible to use tungsten oxide in combination with phosphoric acid distributed in a carrier material such as alumina, silica-alumina or kieselguhr. Similarly, silver or silver promoted with small amounts of copper may be used as a catalyst. When using a silver catalyst, temperatures of 600 to 800°C and pressures of 300 to 800 kPa are preferred. Also, a catalyst mixture comprising iron promoted with molybdenum (18% Fe_2O_3 + 82% MoO_3 by weight) may be employed at temperatures of 350 to 400°C.

In another alternative, the DME product may be converted into liquid fuels, relying upon an olefin intermediate product of DME conversion as feed to the liquid fuels conversion operation. That is, the DME product is converted at a temperature of 343 to 425°C, and preferably at least 370°C, into an olefin intermediate product by contact with a crystalline zeolite represented by HZSM-5 crystalline zeolite. The olefins formed may be branched or straight chained olefins, depending on the conditions employed and the catalyst activity, and may be particularly restricted to boil within the gasoline boiling range. On the other hand, the operating conditions and catalyst may be selected to produce an aromatic-rich gasoline product from the olefins formed. Upgrading the olefin intermediates to a jet fuel product, by the combination of olefin oligomerization or olefination and hydrogenation, is also possible. Oligomerization of the olefin intermediate may be accomplished at a

temperature of 175 to about 250°C, it being preferred to employ a temperature of 200 to 220°C and a pressure of 1000 to 10,000 kPa. When carrying out the oligomerization of olefins to form jet fuel, it is desirable to cofeed water and to maintain about 15% to 18% free P_2O_5 in the catalyst composition. Kieselguhr may be used as the acid catalyst support material.

The synthesis of olefins from the DME product is an intermediate step in a combination of steps leading to the production of various chemical constituents, branched olefins, aromatics and gasoline boiling range materials, depending on reaction conditions and catalyst employed. In addition to the above combinations, it is also recognized that a mixture of olefins from any source, in addition to those produced from DME, may be reacted with methanol to form high octane ethers in the manner provided by published European Patent Application 26041.

In yet another alternative, unreacted syngas is separated from the DME product. The unreacted syngas, normally having a H_2/CO ratio of at least 1, contains substantial amounts of CO_2. Such a syngas composition may be used to advantage in a Fischer-Tropsch syngas conversion operation utilizing iron, cobalt or ruthenium as the Fischer-Tropsch catalyst metal component. In this manner, it is possible to convert the unreacted syngas from the DME synthesis, in a Fischer-Tropsch synthesis operation in the presence or absence of a water-gas-shift metal component.

In any of the processes described above, it is possible to recycle unreacted syngas to the DME conversion operation either before or after CO_2 removal, as required, and with or without the further addition of water to the recycle gas. Also, the total unreacted gas comprising CO_2 may be passed to Fischer-Tropsch syngas conversion operation with or without cofed water and reacted to form a broad spectrum of products, as is known in the art.

The following Examples illustrate the invention. The words "VYCOR" and "PYREX" used in the Examples are registered Trade Marks.

Example 1 - Preparation of Cu/Zn/Al co-precipitated catalyst

To an aqueous solution of the nitrates of aluminum, copper and zinc in molar amounts of 0.115, 0.12 and 0.12, respectively, was added an aqueous solution of 1.05 moles of sodium carbonate. Precipitation was carried out at 85 - 90°C with agitation. The precipitate was cooled, filtered, washed and extracted with water to remove soluble nitrates and carbonates, and then dried in a vacuum oven and calcined for 6 hours at about 280°C.

A dimethyl ether synthesis catalyst was prepared by combining equal weights of the calcined powder and a powdered gamma-alumina, pelletizing the resultant mixture and crushing the pellets to 10-30 mesh.

Example 2 - Preparation of Cu/Zn co-precipitated catalyst (comparison)

Using the procedure of Example 1, a co-precipitated Cu/Zn mixture having a copper/zinc ratio of 1/1, was prepared. The co-precipitated Cu/Zn pair was recovered, washed and dried as described above and then calcined at 343°C.

A DME synthesis catalyst was prepared by combining equal weights of the calcined Cu/Zn powder with a powdered gamma-alumina. The mixture was then pelletized and sized as described in Example 1.

Example 3 - Preparation of Cu/Zn/Al mixed catalyst (comparison)

2 Parts by weight of the Cu/Zn co-precipitated pair prepared in Example 2 were mixed with 1.5 parts by weight of aluminum oxide and the mixture was suspended in water. The suspension was mixed in a blender to prepare a high shear slurry. The mixed solid was recovered and calcined as described above. This is essentially the method of preparation described in U.S. Patent 3,790,505. The ratios of the metal components Cu/Zn/Al were 1/1/1.5, respectively.

The Cu/Zn/Al high shear mixture was then further mixed with powdered gamma-alumina on an equal weight basis, pelletized and sized as described in Examples 1 and 2.

In order to test the catalytic compositions of Examples 1, 2 and 3, there was used a microreactor with related system components which permitted rapid catalyst loading and pretreatment and ready adjustment of reaction conditions, feed gas mixtures and regeneration conditions without disturbing the catalyst. The reactor was 400 mm in length and was made from a 9.5 mm OD 304 stainless steel (SS) tube with an annular 3.2 mm OD 304 SS thermowell running the entire length of the bed of catalyst therein. A 3.0 cc catalyst bed (90 mm long) was centrally positioned in a 300 mm vertical tube furnace. The catalyst bed was held in place by Vycor glass wool supported by Pyrex tubes filling the reactor voids. Temperature was maintained by a proportional band controller with a thermocouple located in the furnace wall near the reactor. During use, premixed H_2 and CO were compressed and fed through activated charcoal traps (the charcoal being necessary to remove traces of iron carbonyl present in the feed gas cylinders). Constant gas flow was maintained by a thermal mass flow controller and reactor pressure was maintained by a back-pressure regulator downstream of the reactor and liquid traps.

All catalysts were initially pretreated in the reactor at 204°C in an H_2/N_2 stream (100 kPa, GHSV = 1500), the hydrogen content of which was slowly increased from 0 to 2 volume percent, then to 8.5%.

The catalyst was cooled in an inert gas stream to a temperature below 49°C, the reactor feed switched to synthesis gas at the space velocity and pressure of the run, and temperature then increased.

Typical run conditions were H_2/CO feed ratio = 1, 10,000 kPa, 315°C, and GHSV = 4000.

Oxidative regeneration of the catalyst was carried out as follows:

1. Depressurize the reactor to atmospheric pressure and flush in helium.

2. Elute a pulse of 100% oxygen from a container of volume 100 liter/liter catalyst (i.e. 100 liters O_2 at STP/liter catalyst) at 100 kPa with helium at a GHSV of about 600 and a temperature of about 288 to 343°C.

3. Flush and pressurize the system to 10,000 kPa with helium.

4. Bring synthesis gas into the reactor to resume reaction at 315°C and 10,000 kPa by passing a 100% syngas stream to the reactor through a "buffer" container of helium at 100 liters per liter of catalyst and at a GHSV of 4000.

Examples 4-6

Using the reactor system described above, each of the catalysts of Examples 1-3 was brought into contact with a syngas feed stream (H_2/CO = 1) at 316°C, 10,000 kPa and GHSV = 4,000. The reactor effluent was analyzed periodically to determine the level of syngas conversion and attempts were made to oxidatively regenerate each of the respective catalysts during the runs. The results obtained are set out in the accompanying drawings as plots of syngas conversion against time on stream for each catalyst.

Curve I represents the behavior of the Cu/Zn/Al co-precipitated catalyst of Example 1. The run was followed for 60 days and the solid points on the curve indicate the oxidative regenerations of the catalyst.

Curve II shows the performance of the Cu/Zn co-precipitated catalyst of Example 2. Again, the solid points indicate attempts at oxidative regeneration of the catalyst. As will be apparent from the plot, the Cu/Zn co-precipitated pair (Curve II) became inactivated much more rapidly than did the Cu/Zn/Al co-precipitated catalyst (Curve I) and, in contrast to the Cu/Zn/Al catalyst, was unaffected by attempts at regeneration.

Curve III shows the result obtained with a Cu/Zn co-precipitated pair which has been physically mixed with Al by high-shear slurry technique (Example 3). As before, the solid points indicate attempts at oxidative regeneration. This catalyst

is seen to behave very similarly to the Cu/Zn co-precipitated pair of Example 2. Physical mixture of the Al with the Cu/Zn pair does not provide the oxidative regenerability shown by the Cu/Zn/Al co-precipitated catalyst of Example 1.

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CLAIMS:

1. A catalyst composition comprising

co-precipitated Cu, Zn and Al components in amounts such that the atomic ratio Al/(Cu+Zn) is not less than 0.1 and the atomic ratio Cu/Zn is from 0.2 to 5.0, and

an acidic dehydrating component.

2. A catalyst composition according to claim 1, wherein the atomic ratio Al/(Cu+Zn) is from 0.1 to 2.0.

3. A catalyst composition according to claim 2, wherein the atomic ratio Al/(Cu+Zn) is from 0.2 to 0.7.

4. A catalyst composition according to any one of claims 1 to 3, wherein the acidic dehydrating component is gamma-alumina; silica-alumina; a porotectosilicate; a clay; a natural or synthetic crystalline aluminosilicate; a crystalline zeolite having a high silica content and a Constraint Index of 1 to 12; a phosphate; or titania in combination with silica, a rare earth or a clay.

5. A catalyst composition according to claim 4, wherein the acidic dehydrating component is gamma-alumina.

6. A catalyst composition according to any one of claims 1 to 5, wherein the acidic dehydrating component comprises from 5 to 95 weight % of the composition.

7. A catalyst composition according to claim 6, wherein the acidic dehydrating component comprises from 20 to 70 weight percent of the composition.

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8. A catalyst composition according to any one of claims 1 to 7, wherein the co-precipitated Cu, Zn and Al components are oxides.

9. A method for converting syngas into an ether product which comprises contacting syngas having a H_2/CO ratio of 0.4 to 3, and water in an amount sufficient to compensate for any hydrogen deficiency in the syngas, with a catalyst composition according to any one of claims 1 to 8 at a temperature of 250 to 400°C, and recovering an ether product in an amount equivalent to at least 10% of the thermodynamic equilibrium conversion of the syngas.

10. A method according to claim 9, wherein the syngas has a H_2/CO ratio of 0.4 to 0.7.

11. A method according to claim 9 or claim 10, wherein the temperature, pressure and space velocity are such that the ether product is obtained in an amount equivalent to at least 50% of the thermodynamic equilibrium conversion of the syngas.

12. A method according to any one of claims 9 to 11, wherein the catalyst is regenerated by contact with an oxygen-containing gas at 250 to 540°C.

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