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UNION CARBIDE CORP *US 4242-103
04.06.79-US-045319 (+889558) (30.12.80) C10k-03/04

Cyclic, two/stage methane prodn. from carbon mon:oxide-contg. gases - by catalytic disproportionation followed by steam conversion of active surface carbon

A cyclic, two-stage process is claimed for the prodn. of methane from CO-contg. gas streams, the method involving (a) passing the gas over a metal catalyst (I) capable of catalysing the disproportionation of CO at 100-350 deg.C and 1-100-atm. to form CO2 and deposit active surface carbon on (I) without forming inactive coke, (b) contacting the active surface carbon layer or (I) with steam or a steam-contg. gas stream at 100-400 deg.C and 1-100 atm. to convert the carbon to methane and CO2, the amt. of methane being at least 50% of stoichiometric and corresponding to a carbon (in the originally decomposed CO) utilisation of at least 12.5%, and (c) passing further CO-contg. gas over (I) and repeating steps (a) and (b) on a cyclic basis.

USES/ADVANTAGES

The process is esp. used in treating effluent streams from the underground gasification of coal with air, from blast furnace operations or the oxygen-blown gasification of coal. A high-pressure methane product stream is obtained without expensive compression equipment or high energy consumption. Prior concn. of CO and/or sepn. of inert gases from it is unnecessary. Catalyst regeneration is not required with each cycle.

DETAILS

The gas stream may contain 5-50 vol.% CO and at least about 5 vol.% nitrogen. Step (a) is pref. effected at 200-350 deg.C and step (b) at 200-350 (pref. about 300) deg.C and 100-500 psi.

(I) comprises Ni, Co, Ru, Re and their alloys, pref. Ni or Co, pref. mixed with a support additive, in amts. of 0.1-50 (pref. 3-30) wt.%, selected from zirconia, alumina and silica, and a binder, in amts. of 5-40 wt.%. The surface area of (I) is at least 25 (pref. at least 50) sq.m. per g. (11pp920).

E(10-J2D) H(9-D) N(2, 3-E).

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UNION CARBIDE CORP *EP ---4-456
23.03.78-US-889558 (03.10.79) C07c-01 C07c-09/04 C10k-03/04

Methane prodn. from carbon monoxide-contg. gas - by disproportionating carbon monoxide to carbon and carbon dioxide, and treating resulting carbon with steam or hydrogen

D/S: E(BE, DT, FR, GB, IT, SW).

Methane prodn. from a CO-contg. gas stream comprises (i) passing the stream over a catalyst which disproportionates the CO to form CO_2 and an active surface carbon, the contact time of the gas stream with the catalyst being such that the active surface carbon is deposited on the catalyst but without subsequently forming inactive coke on it; and (ii) contacting the deposited carbon with (a) steam or a steam-contg. gas stream or (b) hydrogen or a hydrogen-contg. gas stream, thereby converting the active surface carbon to methane and CO_2.

USES/ADVANTAGES

Dilute CO-contg. gas streams (e.g. from underground coal gasification with air, or the effluent from blast furnace operations) can be used without pretreatment to produce low-cost, high-purity methane as a replacement for natural gas. Conversion of the active surface carbon

E(10-J2D)H(9-D) N(2, 3)

with high-pressure (100-500 psi) steam enables a high-pressure methane stream to be generated without expensive compression equipment and high energy consumption

MATERIALS

Pref. the catalyst is chosen from Ni, Co, Fe, Ru, Re and their alloys of surface area $\geq 10\ m^2/g$; esp. Ni of surface area $\geq 25\ m^2/g$. Pref. the catalyst comprises 0.1-50 wt. % of a support additive chosen from zirconia, thoria, alumina, silica and their mixtures. The catalyst is made by coprecipitating the hydroxide or carbonate of the support additive with the hydroxide or carbonate of the catalyst and then reducing the catalyst hydroxide or carbonate to the active catalyst state. The catalyst compsn. may also include 5-40 wt. % of a binding agent.

DETAILS

Pref. CO decomposition and the conversion of active surface carbon to CH_4 takes place at 100-400°C/1-100 atmos.; more pref. the first step takes place at 200-300°C and the second at 200-350°C. Pref. the CO-contg. gas stream contains 5-50 vol. % CO and ≥ 5 vol. % N_2; and it is pref. passed over the disproportionation catalyst

until CO breakthrough occurs in the gaseous effluent from the reaction, thereby enhancing the amt. of active surface carbon deposited while minimising undesired formation of inactive coke. (30pp914).
(E) ISR: US2544574; US3511624.