Claims

1. A method for production of methanol comprising the steps of: reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide; synthesizing methanol by reaction of the syngas obtained in the reforming step in the presence of a catalyst; recycling by separating the methanol synthesized in the methanol synthesis step from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas; and separating hydrogen by separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas.

2. The method for production of methanol according to claim 1, wherein a PSA unit is used for the separation of the hydrogen gas.

3. The method for production of methanol according to claim 1 or 2, wherein a raw material gas in the reforming step has a steam/carbon ratio of 0.7 or more but 1.7 or less.

4. The method for production of methanol according to any of claims 1 to 3, wherein the syngas obtained in the reforming step has a carbon activity of 0.36 or more but 1.0 or less.

5. The method for production of methanol according to any of claims 1 to 4, wherein the catalyst used in the reforming step has a MgO calcined at 1,000°C or more but 1,500°C or less and Ru and/or Rh loaded thereon in an amount of 200 wtppm or more but 2,000 wtppm or less.

6. The method for production of methanol according to

any of claims 1 to 5, wherein the catalyst used in the reforming step has a support having a specific surface area of 0.1 m^2/g or less.

7. The method for production of methanol according to any of claims 1 to 6, wherein the reaction conditions in the reforming step are an outlet reaction temperature of 850°C or more but 950°C or less, a reaction pressure of 1.0 MPaG or more but 3.0 MPaG or less, the GHSV thereof of 2,000 hr^{-1} or more but 10,000 hr^{-1} or less, and the CO_2/carbon ratio of the raw material gas thereof of 0.1 or more but 0.6 or less.

8. The method for production of methanol according to any of claims 1 to 7, wherein the gas after merging the hydrogen gas with the syngas has an R value of from 1.8 to 2.2, and the residual gas after separating the hydrogen gas in the hydrogen separation step is utilized as a heat source for the reformer.

9. A method for production of an acetic acid raw material or an MMA raw material, which comprises the method for the production of methanol according to any of claims 1 to 8, further comprising the step of separating carbon monoxide by extracting a part of the syngas obtained in the reforming step and separating carbon monoxide from the part of the syngas, and a residual syngas after the extraction of the part of the syngas is fed to the methanol synthesis.

10. The method for production of an acetic acid raw material or an MMA raw material according to claim 9, wherein the carbon monoxide separation step comprises the steps of: removing CO_2 gas from the part of the syngas; and cryogenically separating

carbon monoxide from a CO_2-removed gas by a cryogenic separation process.

11. The method for production of an acetic acid raw material or an MMA raw material according to claim 10, wherein the CO_2 gas removed in the CO_2 removing step is fed to an upstream side of the reforming step for recycle.

12. A methanol production apparatus comprising: a reformer for reforming a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide; a methanol reactor for synthesizing methanol by reaction of the syngas obtained in the reformer in the presence of a catalyst; a recycle unit for separating the methanol synthesized in the methanol reactor from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas; and a hydrogen separation unit for separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas.

13. A plant for production of an acetic acid raw material or an MMA raw material, which comprises the methanol production apparatus according to claim 12, further comprising a carbon monoxide separation unit for extracting a part of the syngas obtained in the reformer and separating carbon monoxide from the part of the syngas, and supplying a residual syngas after the extraction of the part of the syngas to the methanol reactor.

14. A method for remodeling a methanol plant including a reformer, which is filled with a steam reforming catalyst, for

producing an acetic acid raw material or an MMA raw material in addition to methanol, the method comprising replacing the steam reforming catalyst in the reformer with a CO_2 reforming catalyst so as to reform lower hydrocarbon gas with carbon dioxide and steam, and providing a facility for separating carbon monoxide from a part of syngas obtained by the reforming.

CLAIMS

1. A method for production of methanol comprising the steps of:

Reforming a raw material gas of a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide;

synthesizing methanol by reaction of the syngas obtained in the reforming step in the presence of a catalyst;

recycling by separating the methanol synthesized in the methanol synthesis step from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas; and

separating hydrogen by separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas;

wherein the raw material gas in the reforming step has a steam/carbon ratio in a range of 0.7 or more but 1.7 or less and the catalyst used in the reforming step excludes Ni-based catalysts that are likely to cause carbon deposition in the range.

2. The method for production of methanol according to claim 1, wherein a PSA unit is used for the separation of the hydrogen gas.

3. The method for production of methanol according to claim 2, wherein the syngas obtained in the reforming step has a carbon activity of 0.36 or more but 1.0 or less.

4. The method for production of methanol according to claim 3, wherein the catalyst used in the reforming step has a MgO calcined at 1,000°C or more but 1,500°C or less and Ru and/or Rh loaded thereon in an amount of 200 wtppm or more but 2,000 wtppm or less.

5. The method for production of methanol according to claim 4, wherein the catalyst used in the reforming step has a support having a specific surface area of 0.1 m^2/g or less.

6. The method for production of methanol according to claim 5, wherein the reaction conditions in the reforming step are an outlet reaction temperature of

850°C or more but 950°C or less, a reaction pressure of 1.0 MPaG or more but 3.0 MPaG or less, the GHSV thereof of 2,000 hr^{-1} or more but 10,000 hr^{-1} or less, and the CO2/carbon ratio of the raw material gas thereof of 0.1 or more but 0.6 or less.

7. The method for production of methanol according to claim 6, wherein the gas after merging the hydrogen gas with the syngas has an R value of from 1.8 to 2.2, and the residual gas after separating the hydrogen gas in the hydrogen separation step is utilized as a heat source for the reformer.

8. A method for production of an acetic acid raw material or an MMA raw material, which comprises the method for the production of methanol according to claim 1, further comprising the step of separating carbon monoxide by extracting a part of the syngas obtained in the reforming step and separating carbon monoxide from the part of the syngas, and a residual syngas after the extraction of the part of the syngas is fed to the methanol synthesis.

9. The method for production of an acetic acid raw material or an MMA raw material according to claim 8, wherein the carbon monoxide separation step comprises the steps of: removing CO2 gas from the part of the syngas; and cryogenically separating carbon monoxide from a CO2-removed gas by a cryogenic separation process.

10. The method for production of an acetic acid raw material or an MMA raw material according to claim 9, wherein the CO2 gas removed in the CO2 removing step is fed to an upstream side of the reforming step for recycle.

11. A methanol production apparatus comprising:

a reformer for reforming a raw material gas of a lower hydrocarbon gas containing steam and carbon dioxide added thereto in the presence of a catalyst to generate syngas mainly including hydrogen and carbon monoxide;

a methanol reactor for synthesizing methanol by reaction of the syngas obtained in the reformer in the presence of a catalyst;

a recycle unit for separating the methanol synthesized in the methanol reactor from a residual gas containing unreacted gas and merging the residual gas as a recycle gas with the syngas; and

a hydrogen separation unit for separating hydrogen gas from at least a part of the recycle gas and merging the hydrogen gas with the syngas;

wherein the raw material gas in the reformer has a steam/carbon ratio in a range of 0.7 or more but 1.7 or less and the catalyst used in the reformer excludes Ni-based catalysts that are likely to cause carbon deposition in the range.

12. A plant for production of an acetic acid raw material or an MMA raw material, which comprises the methanol production apparatus according to claim 11, further comprising a carbon monoxide separation unit for extracting a part of the syngas obtained in the reformer and separating carbon monoxide from the part of the syngas, and supplying a residual syngas after the extraction of the part of the syngas to the methanol reactor.

13. A method for remodeling a methanol plant including a reformer, which is filled with a steam reforming catalyst, for producing an acetic acid raw material or an MMA raw material in addition to methanol, the method comprising the steps of:

replacing the steam reforming catalyst in the reformer with a CO2 reforming catalyst so as to reform lower hydrocarbon gas with carbon dioxide and steam;

providing a facility for separating carbon monoxide from a part of a syngas obtained by the reformer; and

providing a hydrogen separation unit for separating a hydrogen gas from at least a part of a recycle gas of the methanol plant and merging the hydrogen gas with a syngas supplied to the methanol plant,

wherein the CO2 reforming catalyst excludes Ni-based catalysts that are likely to cause carbon deposition when a raw material gas to the CO2 reforming catalyst has a steam/carbon ratio in a range of 0.7 or more but 1.7 or less.