

PURIFICATION OF A MIXTURE OF H₂/CO BY CATALYSIS OF THE
NO_x

5 The invention relates to a method for purifying
gas mixtures, particularly gas mixtures mainly
containing hydrogen and carbon monoxide, commonly
called H₂/CO mixtures or "syngas", and, optionally,
methane (CH₄), which are polluted by impurities of the
10 NO_x type.

The H₂/CO gas mixtures can be obtained in various
ways, particularly:

15 - by reforming with steam or CO₂, by partial
oxidation,

 - by mixed methods, such as the ATR (Auto Thermal
Reforming) method, which is a combination of steam
reforming and partial oxidation, using gases such as
methane or ethane, or

20 - by coal gasification or recovered as waste gases
downstream of acetylene production plants.

The proportion of CO in these H₂/CO mixtures varies
according to the operating conditions typically between
25 about 5 and 30% by volume. Moreover, besides the
hydrogen and CO, the compounds CH₄, CO₂, and H₂O are
often comprised in the mixture, and in variable
proportions.

30 At present, several alternatives are available for
upgrading H₂/CO mixtures, that is, particularly by
producing:

 - pure hydrogen, which has many applications,
 - pure CO, which is used in particular for the
35 synthesis of acetic acid and phosgene, which is a
reaction intermediate in the production of
polycarbonates, or

- an oxo-gas, which is a purified H₂/CO mixture enriched with CO (> 45% by volume) useable for the synthesis of butanol.

5 For this purpose, it is necessary first to purify the H₂/CO mixtures.

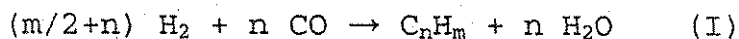
However, it may also be necessary to purify the H₂/CO mixtures for the needs of their downstream use, by means of specific reactions that can be carried out using specific catalysts and/or adsorbents for a particular impurity or by any other suitable chemical treatment.

15 Moreover, the removal of certain impurities present in the gas streams is difficult at the industrial level.

In fact, the catalytic reactions serving to remove the impurities must not cause the H₂/CO gas mixture to be purified to react, or as little as possible.

The reactivity of H₂/CO mixtures is well known.

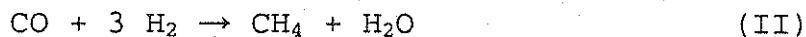
25 Thus, the Fischer-Tropsch synthesis has been used for several years to obtain hydrocarbons by the following reaction mechanism (I):



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A variant concerns the formation of methane, called methanation, as described by G. A. Mills et al, Catalysis Review, vol. 8, No. 2, 1973, p. 159 to 210, reflected by the following reaction (II):

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Furthermore, carbon monoxide can also decompose by the following Boudouard reaction (III):



5 In general, numerous metals can be used to catalyze the formation of hydrocarbons from CO and H₂. Examples include the following metals: Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd, or Ag as explained by F. Fischer, H. Tropsch and P. Diltthey, Brennst-Chem, vol. 6, 1925, p. 265.

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The methanol formation reaction is also carried out on numerous metals, including copper:



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Thus, the ethylene hydrogenation catalysts that are commonly based on platinum deposited on alumina lead to a Fischer-Tropsch reaction (reaction (I) above) with the formation of hydrocarbons, particularly ethylene, which is found to be more concentrated at the reaction outlet than at the inlet, that is, in the gas before reaction.

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Similarly, certain oxidation catalysts cause the formation of methanol that must then be removed downstream of the catalyst bed.

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In other words, these supplementary reactions have the consequence of generating additional reaction products, not present in the initial gas to be purified, which must be removed by adsorption downstream, in addition to the virtually unavoidable pollutants present in the initial gas.

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The undesirable impurities include nitrogen oxides commonly called NO_x.

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The NO_x comprise the following compounds: N₂O, NO, N₂O₃, NO₂, N₂O₅. The latter three compounds are highly

reactive and react spontaneously with reducing agents such as H_2 and CO , to form N_2 , CO_2 , and H_2O . NO and N_2O species, which are more stable, may be present in the H_2/CO mixture. If this mixture must be treated in a cold box (cryogenic distillation method), their presence incurs a potential danger. In fact, in the presence of traces of O_2 and unsaturated hydrocarbons, NO_x can form products that are liable to accumulate in the cryogenic distillation units and damage these units. It is therefore indispensable to be able to remove them as efficiently as possible.

In other words, obtaining an efficient removal of nitrogen oxides, commonly called NO_x , from the gas streams, in particular from the H_2/CO streams, while limiting the production of undesirable by-products, is vitally important but not easy to achieve industrially.

The problem that arises is accordingly to produce and recover a gas stream, particularly of H_2/CO , stripped of most and preferably all of the NO_x impurities it contains.

In other words, the goal of the invention is to improve the methods of the prior art for purifying gas mixtures, particularly of the H_2/CO type, by proposing an efficient method for purifying an H_2/CO mixture of the NO_x impurities it contains, in order to prevent their concentration in the cryogenic distillation units.

The object of the present invention is to provide a method for purifying a gas stream containing at least one nitrogen oxide (NO_x) as impurities, in which the gas stream is contacted with at least one catalyst containing copper or palladium, at a temperature of between $100^\circ C$ and $200^\circ C$, in order to catalyze at least part of the nitrogen oxide.

Depending on each case, the method of the invention is to provide a method of purification of a mixture of H_2/CO by catalyst of the NO_x may comprise one or more of the following technical characteristics:

- the temperature is between $120^\circ C$ and $180^\circ C$ and/or the pressure is between 10 and 80 bar, preferably about 40 to 55 bar,

- the Gas Hourly Space Velocity is between 1000 and 10 000 Sm^3/h of gas/ m^3 of catalyst, preferably between 2000 and 6000 Sm^3/h of gas/ m^3 of catalyst (1 $Sm^3 = 1 m^3$ considered at $0^\circ C$ and 1 atm),

- the gas stream is contacted with the catalyst containing copper,

- the gas stream contains hydrogen (H_2) and carbon monoxide (CO), and optionally methane (CH_4),

- the nitrogen oxides are converted to water (H_2O), O_2 , NH_3 and/or nitrogen,

- the water (H_2O) and NH_3 resulting from the catalysis of the NO_x are removed by means of one or more adsorption steps,

- at least one adsorption step is carried out using one or more adsorbents selected from the group formed by zeolites, exchanged or not, activated aluminas, silica gels, or mixtures or combinations thereof,

- the gas stream to be separated contains 10% by volume to 90% by volume of H_2 , 10% by volume to 90% by volume of CO and optionally, methane,

- the catalyst may be protected by at least one protective bed located upstream of said catalyst. The protective bed serves to protect the catalyst from chemical species liable to be present in the gas, in addition to the nitrogen oxides, and liable to degrade or decrease the activity of the catalyst, for example mercury (Hg), arsenic (AsH_3), sulfur compounds (H_2S , thiols, thioethers), halogenated compounds (HBr , HCl , organic halides), HCN , iron carbonyl $Fe(CO)_5$ and nickel carbonyl $Ni(CO)_4$. The protective bed may comprise one or more adsorbents, for example the product PICATOX Cu/Ag from PICA,

- the catalyst used in the framework of the invention may be in the form of particles ranging from 0.20 to 1 cm in size.

5 The volume of catalyst to be used depends on the concentration of the impurities to be removed and the properties of the specific products.

10 The volumes of adsorbents and catalysts are given for guidance, because they depend on the concentration of the impurities to be removed and on the properties of the specific products. In general, it can be considered that for a given case, the quantity of adsorbent to be used is approximately proportional to
15 the quantity of pollutant to be removed, while the quantity of catalyst is approximately proportional to the contact time or to the inverse of the Gas Hourly Space Velocity (GHSV) which is the volume of gas to be treated per hour, related to the volume of catalyst.
20 The volume of gas can be related to the reactor inlet pressure (the GHSV then depends on the pressure), or can be expressed in defined conditions, at 1 bar and 0°C for example (the GHSV then does not depend on the pressure); some leeway exists in the choice of the
25 reference conditions appropriate to each application. The contact time and GHSV^{-1} are only approximately proportional because the contact time, in addition to the pressure, depends on the temperature along the column, the variation of the number of moles during the
30 reaction, and the pressure drop. However, for a given set of reaction conditions, the two parameters can be selected at will.

35 Another parameter to be taken into account is the content of impurities to be removed at the outlet of the gaseous effluents. On the whole, the lower the desired content, the higher the quantity of catalyst.

Illustrative Example

To check the efficiency of the method of the invention, an H_2/CO gas mixture was contacted with catalysts according to the invention, that is, a copper (Cu) catalyst and a palladium (Pd) catalyst.

The copper-based catalyst was the product reference 0860T from Engelhard.

The palladium-based catalyst was the product reference 4586 from Engelhard.

In each test, the NO_x were catalyzed at a pressure of 47 bar and a temperature of about 120 to 180°C.

The initial gas contained about 80% by volume of H_2 and CO , the remainder consisting particularly of methane and NO_x impurities (about 0.15% by volume) to be removed.

During these tests, the space velocity adopted was 5000 to 2500 $Sm_3/h/m_3$ of catalyst (for example, 6 to 12 m^3 of catalyst to treat 30 000 Sm^3/h of gas).

Table

Test No.	NOx contents of gas (in mole ppb)		
	At reactor inlet	At outlet with Pd catalyst	At outlet with Cu catalyst
1	398	21	<10
2	1222	178	<10
3	1175	184	<10
4	3410	245	<10
5	1049	170	<10
6	1170	138	<10

7	1317	100	<10
8	1489	91	<10
9	521	42	<10
10	1889	60	<10
11	882	20	<10
12	962	71	<10
13	2326	47	<10
14	2736	59	<10
15	1672	48	<10
16	819	62	<10
17	1225	171	<10

The above table shows that the use of a copper or palladium catalyst is effective for catalyzing the NOx to reaction products such as NH₃, N₂, O₂ and H₂O, species
5 that are easier to remove subsequently, or which raise no problem for the downstream unit.

The copper catalyst allows a more efficient removal of the NOx (residual quantity after
10 purification <10 ppb on each test) than the palladium catalyst, as the catalytic activity of the latter may be slightly reduced if the CO content is high.

Despite this, on gas streams poor in CO but
15 containing species of the diene type, it may be more advantageous to use a palladium catalyst than a copper catalyst, because palladium serves to convert the diene species, whereas copper does not achieve this as effectively.

CLAIMS

1. A method for purifying a gas stream containing hydrogen (H_2) and carbon monoxide (CO), and further containing at least one nitrogen oxide (NO_x) as impurities, in which the gas stream is contacted with at least one catalyst containing copper and/or palladium, at a temperature of between $100^{\circ}C$ and $200^{\circ}C$, in order to remove at least part of the nitrogen oxide.
2. The method as claimed in claim 1, wherein the exhaust gas in contact with a catalyst is at a temperature of between $120^{\circ}C$ and $180^{\circ}C$ and/or at a pressure of between 10 and 80 bars.
3. The method as claimed in claim 1 or claim 2, wherein the exhaust gas in contact with a catalyst has a Hourly Space Velocity of between 1000 and $10000\text{ Nm}^3/\text{h}/\text{m}^3$ of catalyst.
4. The method as claimed in one of claims 1 to 3, characterized in that the gas stream is contacted with the catalyst containing copper.
5. The method as claimed in one of claims 1 to 4, characterized in that the gas stream contains hydrogen (H_2), carbon monoxide (CO), and methane (CH_4).
6. The method as claimed in one of claims 1 to 5, characterised in that the nitrogen oxides are converted to water (H_2O), O_2 , NH_3 , and/or N_2 .
7. The method as claimed in claim 6, characterized in that H_2O and NH_3 resulting from catalysis of the NO_x are removed by means of one or more adsorption steps.

8. The method as claimed in claim 7, characterized in that at least one adsorption step is carried out using one or more adsorbents selected from the group formed by zeolites, exchanged or not, activated aluminas, silica gels, or mixture or combinations thereof.

9. The method as claimed in one of claims 1 to 4, characterized in that the gas stream to be separated contains 10% by volume to 90% by volume of H₂, 10% by volume to 90% by volume of CO and optionally, methane.

10. The method as claimed in one of claims 1 to 9, characterized in that the catalyst is protected by at least one protective bed located upstream of said catalyst.

11. The method as claimed in claim 1, wherein the exhaust gas in contact with a catalyst is at a temperature of between 120 °C and 180 °C and/or at a pressure of between 20 and 50 bars.

12. The method as claimed in claim 1 or claim 2, wherein the exhaust gas in contact with a catalyst has a Hourly Space Velocity of between 2000 and 6000 Nm³/h/m³ of catalyst.