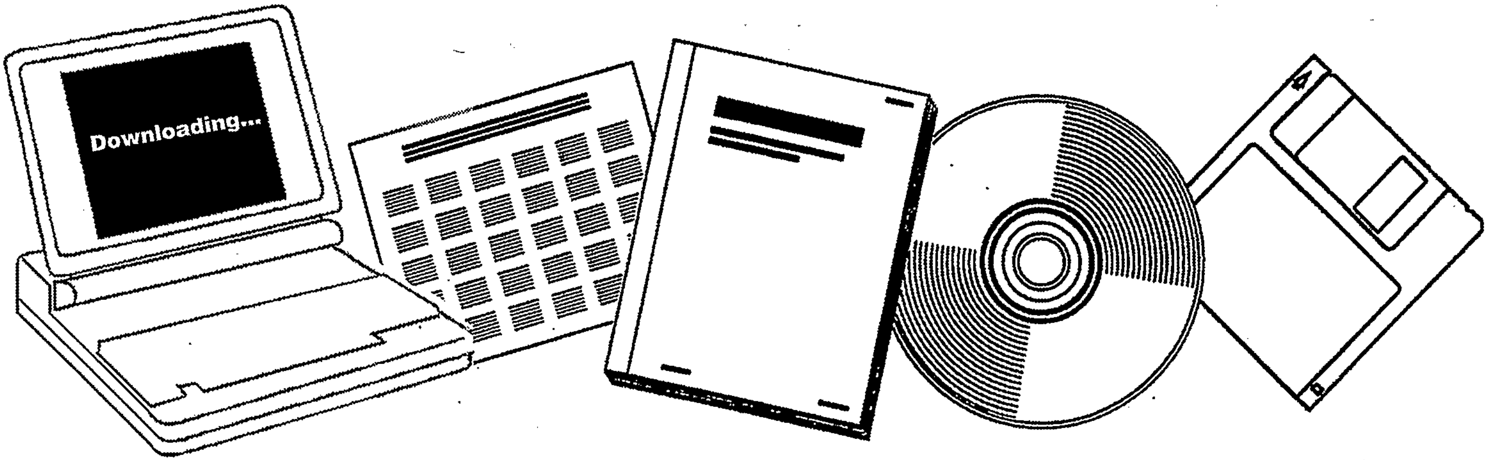
PB82118563

METHANATION CATALYSTS

INTERNATIONAL ENERGY AGENCY COAL
RESEARCH, LONDON (ENGLAND)

1980



One Source. One Search. One Solution.

NTIS

Providing Permanent, Easy Access to U.S. Government Information

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

Search the NTIS Database from 1990 forward

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on **www.ntis.gov.** You now have access to information on more than 600,000 government research information products from this web site.

Link to Full Text Documents at Government Web Sites

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

Download Publications (1997 - Present)

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

www.ntis.gov

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161

PB82118563

Methanation catalysts

G. H. Watson

Report number ICTIS/TR 09
February 1980
IEA Coal Research, London

IEA Coal Research
14/15 Lower Grosvenor Place
London SW1W 0EX

ISBN 92-9029-053-6

IEA COAL RESEARCH

TECHNICAL INFORMATION SERVICE

This report is one of a series produced by the Technical Information Service of IEA Coal Research. It has been reviewed in draft form by the appropriate experts in Member Countries and their comments have been taken into consideration. This document has been approved for distribution by the Executive Committee of the Technical Information Service.

IEA Coal Research is part of the International Energy Agency (IEA) which was founded in 1974 by member countries of the Organization for Economic Cooperation and Development (OECD). The purpose of the IEA is to explore means by which countries interested in minimising their dependence on imported oil can cooperate. Particular member nations were asked to take the initiative in organizing collaboration in the various fields of research and development and the UK was invited to take the lead in establishing the Coal Working Group, covering coal technology. IEA Coal Research was set up in 1975 and covers five projects, the Fluidised Bed Combustion Project, Economic Assessment Service, Technical Information Service, World Coal Reserves and Resources Data Bank Service, Mining Technology Clearing House.

The Technical Information Service is supported by fourteen countries: Austria, Belgium, Canada, Denmark, the Federal Republic of Germany (FRG), Ireland, Italy, Japan, the Netherlands, New Zealand, Spain, Sweden, the UK and the USA. The Service accepts enquiries from members, ranging from simple fact finding to the preparation of bibliographies and critical reviews. Regular features of the Service will be the production of critical reviews and executive surveys of the literature on subjects of general interest to coal producers and consumers, including environmental problems. The Service also produces Coal Abstracts, a monthly abstracts journal with comprehensive world-wide coverage of all journal and report literature and conference proceedings in the field of coal science and technology, from the mining of the coal to its ultimate uses.

General enquiries on the Service should be addressed to:

I.H. Hogg M.B.E.
Head of Technical Information Service
IEA Coal Research
14/15 Lower Grosvenor Place
London SW1W 0EX

Telephone: 01-828-4661 Telex: 917624 Niceba G

Specific technical enquiries in connection with this report should be addressed to the author at the above address.

Summary

Although all the Group VIII metals are catalytically active in the hydrogenation of carbon monoxide to form methane ("methanation"), nickel, despite extensive investigations of alternative materials, remains the favoured catalyst for the reaction by virtue of its life, high activity, selectivity towards methane formation in preference to other hydrocarbons, and its comparatively low cost. Sensitivity to poisoning by sulphur is the main disadvantage of nickel catalysts. Some sulphur-resistant materials catalyse the methanation reaction, but are much less active than nickel.

Much of the recent literature on methanation catalysts is concerned with preparative techniques and the nature of catalyst supports, factors markedly affecting catalyst properties.

The mechanism of methanation catalysis is not yet completely established; this review contains a list of the most feasible theories.

The review also presents suggestions that have been made for further research into methanation catalysts.

Contents

List of tables

1. Introduction

Reaction between hydrogen and carbon monoxide can lead to a variety of useful products depending on reaction conditions, ratio of the gases in the feed and the type of catalyst. Although the processes may be technically feasible, at present they are not all commercially viable. Among the reactions of greatest interest are those producing methane ($3H_2 + CO \rightleftharpoons CH_4 + H_2O$), paraffins ($(2n+1)H_2 + nCO \rightleftharpoons C_nH_{2n+2} + nH_2O$), alcohols, especially methanol ($2nH_2 + nCO \rightleftharpoons C_nH_{2n+1}OH + (n-1)H_2O$), and olefins ($2nH_2 + nCO \rightleftharpoons C_nH_{2n} + nH_2O$). Since mixtures of hydrogen and carbon monoxide derive from water gas, the reactions provide methods of manufacturing products from fossil fuels and particularly a means of increasing the amount of hydrogen combined with carbon in coal, which is hydrogen-deficient compared with petroleum.

Currently, the synthesis of methane from hydrogen and carbon monoxide ("methanation") is receiving particular attention because it is an essential step in one process for the manufacture of that gas from coal, a process likely to be commercially operable in the future when it becomes necessary to meet dwindling reserves of natural gas in the North Sea and elsewhere by a substitute natural gas (SNG). The process comprises

1. total gasification of coal in steam, perhaps with oxygen, basically $C+H_2O \rightleftharpoons H_2 + CO$);
2. adjustment of the ratio of hydrogen to carbon monoxide in the product gas by the water gas shift reaction and removal of carbon dioxide as necessary (basically $CO+H_2O \rightleftharpoons H_2 + CO_2$);
3. catalytic conversion of the hydrogen and carbon monoxide to methane after removal of any deleterious materials (such as hydrogen sulphide) in the reaction gas ($CO+3H_2 \rightleftharpoons CH_4+H_2O$). Although the optimum molecular ratio of hydrogen to carbon monoxide is 3: 1 in some cases it may be economically advantageous to use a lower ratio.

Methanation is practised also for another purpose. In the manufacture of ammonia by the catalytic reaction of hydrogen and nitrogen the content of oxides of carbon in the synthesis gas must be reduced to a very low level to prevent catalyst poisoning. To effect this, after conversion of carbon monoxide to carbon dioxide by water gas shift and absorption of the latter, residual oxides of carbon are removed by methanation, a simple and relatively inexpensive process. The methane produced is inert to ammonia synthesis catalysts.

In the application of methanation to produce SNG the reaction mixture of hydrogen and carbon monoxide will contain probably 30% to 50% of the monoxide, whereas in "purification" methanation very low concentrations of carbon oxides are hydrogenated. Under the latter conditions at least, catalysts effective for carbon monoxide hydrogenation are generally also effective for the hydrogenation of carbon dioxide (Randhava and Rehmat 1970, Kreindel and others 1972b), although it has been reported in a paper dealing with the kinetics of the reactions $4H_2+CO_2=CH_4+2H_2O$ and $3H_2+CO= CH_4+H_2O$ that over a nickel catalyst at 200°C carbon monoxide even in low concentration markedly reduces the methanation rate of carbon dioxide (Van Herwijnen and others 1973). In this review catalysts intended for the removal of carbon oxides in low concentration from other gases ("purification" methanation) are considered in a separate section. It is hoped that this arrangement, although entailing some repetition, will be helpful to the Reader.

Methanation, $CO+H_2O \rightleftharpoons H_2+CO_2$); is apparently a comparatively simple reaction, and most of the thermodynamic data are readily available in the literature, but the detailed mechanism of the reaction over catalysts has not been established entirely unambiguously. Equilibrium constants for the reaction, calculated from thermodynamic data, are given in Table 1 (Imperial Chemical Industries Ltd 1970), which shows that, thermodynamically at least, the forward reaction is favoured by low temperature and raised pressure.

Table 1. Equilibra for reactions $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$ $CO_2 + 4H \rightleftharpoons CH_4 + 2H_2O$

(Imperial Chemical Industries Ltd. 1970)

Equilibrium constants,

$$Kp_{CO} = \frac{p_{CH_4} \cdot p_{H_2O}}{p_{CO} \cdot p^3 H_2}$$

$$Kp_{CO_2} = \frac{p_{CH_4} \cdot p^2 H_2O}{p_{CO_2} \cdot p^4 H_2}$$

Temp.	Kp_{CO}	Kp_{CO_2}
200	0.21547×10^{12}	0.94748×10^{9}
220	0.23473×10^{11}	0.15589×10^{9}
240	0.30353×10^{10}	0.29435×10^{8}
260	0.45626×10^{9}	0.62706×10^{7}
280	0.78369×10^{8}	0.14863×10^{7}
300	0.15161×10^{8}	0.38747×10^{6}
320	0.32635×10^{7}	0.11001×10^{6}
340	0.77350×10^{6}	0.33737×10^{5}
360	0.20004×10^{6}	0.11094×10^{5}
380	0.56011×10^{5}	0.38882×10^{4}
400	0.16862×10^{5}	0.14442×10^{4}
420	0.54247×10^{4}	0.56582×10^{3}
440	0.18550×10^{4}	0.23282×10^{3}
460	0.67099×10^{3}	0.10023×10^{3}
480	0.25564×10^{3}	0.44995×10^{2}
500	0.10219×10^{3}	0.20997×10^{2}
520	0.42710×10^{2}	0.10157×10^{2}
540	0.18605×10^{2}	0.50814×10^{1}
560	0.84234×10^{1}	0.26225×10^{1}
580	0.39532×10^{1}	0.13936×10^{1}
600	0.19186×10^{1}	0.76104×10^{1}

The reaction between carbon monoxide and hydrogen over a nickel catalyst to produce methane was first reported by Sabatier and Senderens (1902, 1905) in the early part of this century, and since then, despite much research, nickel had continued as the major catalyst for the reaction because of its high activity, selectivity for methane formation and low cost (Atkinson and Nicks 1976a).

Methanation catalysts operate for long periods and in large catalyst beds. Catalyst life and strength are, therefore, of more importance than initial activity (although, of course, this must be adequate), and the major problems are those connected with factors causing or contributing to catalyst decay, notably (i) sulphur poisoning, (ii) loss of activity due to too low thermal stability, (iii) carbon deposition (Vannice 1976a, McArthur 1977b). These have been considered in detail by Cusumano, Dalla Betta and Levy (1976, pp459-468), whose conclusions are summarised below.

(i) Sulphur poisoning.

Methanation catalysts in general are very sensitive to sulphur poisoning. In the case of nickel catalysts, for example, the adsorption of sulphur from the feed gas is almost quantitative and the sulphided catalyst is inactive for methanation. The mechanism may be complex. Adsorbed sulphur poisons by competing with reactants for active sites on the catalyst surface, but often the effect is greater than can be accounted for by simple loss of active surface area, and it has been suggested that it is due to reconstruction of the catalyst surface (Cusumano and others 1976, p 94).

Additives to and particle size of a catalyst can affect its sulphur tolerance.

Table 2, due to Cusumano, Dalla Betta and Levy (1976, p461), shows the expected life of a high loading Ni/Al_2O_3 catalyst in reaction gases containing various proportions of H_2S. Bases for the calculations are shown in the table. It was assumed that the catalyst must be replaced when 50% of the bed is sulphided, and the table shows the time required (a) to sulphide 50% of the Ni surface, (b) to convert 50% of the bulk nickel to nickel sulphide. In reality, catalyst replacement would probably be necessary before 50% sulphidation because of low productivity.

Table 2. Calculated catalyst lifetime in sulphur-containing streams *(Cusumano and others 1976, p.461)*

Basis of calculation:

Process: Gas space velocity: 10,000h^{-1}
Catalyst deactivated and replaced at 50% sulphidation

Catalyst: Ni/Al_2O_3 with 25% Ni
Apparent bulk density: 1 g/cm^3
Ni dispersion (i.e. ratio of surface nickel to total nickel in catalyst) : 0.25

Type of sulphidation	Bulk 50% NiS			Surface 50% Ni		
H_2 conc. in reaction gases, ppm	10	1	0.1	10	1	0.1
Catalyst life, days	20	200	2000	5	50	500

From Table 2 it appears that the life of a nickel methanation catalyst is adequate for a practical process only when the level of H_2S in the reaction gases does not exceed perhaps 1 ppm. Data obtained from methanation in a pilot plant at Sasol, South Africa, compare to the estimates shown in Table 2 (Cusumano and others 1976, p 460). With a supported nickel catalyst a level of 0.05 ppm of H_2S in the reaction gases resulted in slow deactivation of the initial portion of the catalyst bed but no deactivation further into the bed even after fifty days on stream. A level of 3 ppm of H_2S in the gases caused very rapid deactivation much further into the catalyst bed after only six days of operation.

The above authors point out that at the temperature of most methanation processes (300° – 450°C) bulk nickel sulphide is not stable in a reaction stream containing 60% hydrogen with a level of 1 ppm H_2S (i.e. a ratio of H_2S/H_2 of 2×10^{-6}): the observation that a surface sulphide layer on nickel is stable to much lower H_2S/H_2 ratios indicates that deactivation of Ni by sulphur is probably due to strong adsorption of H_2S. The form of a nickel catalyst does not appear to have much effect on its sulphur tolerance or sulphur capacity.

At present no straightforward or economic method of regenerating sulphur-poisoned nickel catalysts is known, although as indicated in Section 2.8, it may prove possible to regenerate certain metal catalysts used in suspension in molten metal salts. As stated later in this review, molybdenum and tungsten sulphides are not poisoned by sulphur, but they are less reactive methanation catalysts than some other materials and require higher reaction temperatures.

(ii) Thermal stability.

The high exothermicity of methanation is an important factor in considering techniques and plant for operating the process, because if the reaction temperature becomes too high not only is the equilibrium state of the hydrogenation reaction adversely affected but the catalyst life is shortened by sintering of the metal particles. The process can be operated in two basically different ways. In one, reaction temperature is kept low by process technique; in the other the process is operated adiabatically without temperature control, the maximum temperature depending on the conversion limit. Methods of controlling temperature in the first system include product gas recycle, addition of steam, tube-wall reactor designs, use of a liquid phase heat removal medium and fluidization. These techniques are referred to later in the text in connection with catalysts described for them; a few recent papers concerned primarily with technique and only cursorily with catalysts have been noted but not reviewed (Blum and others 1974, Diehl and others 1974, Sherwin and others 1975, Alpert and others 1976, Sidel' nikov 1976, Moeller and Heinz 1976, Takenaka and others 1977, Moeller and others 1976, Kato and others 1976, Haynes and others 1972).

Reaction temperature in either method of operation lies between 300° and 450°C, at which with the exercise of care catalyst life and activity are adequate, although, of course, any improvement in these is advantageous. However, catalysts capable of operation at higher temperature are desirable. This is because (within limits) the higher the temperature at which the heat of methanation is released the more effectively can it contribute to overall thermal efficiency of the conversion process, for example of coal to SNG. Also, sulphur poisoning may be less of a problem at higher temperature because of decreased stability of catalyst metal sulphide under the conditions of operation.

(iii) Carbon deposition.

In actual use uncontaminated nickel catalysts operating at up to 450°C with 20% to 50% mole H_2O in the methanation reactants maintain activity for prolonged periods when the H_2/CO ratio varies from 5.8 to 2.0. Although, as stated in Section 2.10, reactive carbon may play an important role in the methanation reaction, under certain transient conditions or at higher temperature (or even at 400°C in the absence of added water) bulk carbon in unreactive form or as Ni_3C, produced on or in the catalyst, can lead to loss of catalyst activity and fouling of equipment (Dalla Betta and Shelef 1976).

Mohnot and Kyle (1978) have determined the conditions for carbon deposition from various gas compositions by considering gas-phase/solid carbon equilibria for the system comprising carbon, hydrogen, oxygen, nitrogen over the range of conditions 500–1500 K, 100 to 2500 kPa, O/H atomic ratios 0.001 to 1000 and N/O atomic ratios 0 to 10.

White and others (1975) have calculated the equilibrium constants of reactions between hydrogen, oxides of carbon, carbon, methane and steam, and described how the deposition of bulk carbon in SNG manufacture can be avoided by control of the water gas shift reaction.

However, conditions may arise in which the deposition of unreactive carbon on catalysts cannot be avoided, and attention has been given to its removal. Bernardo and Trimm (1979) studied the kinetics of gasification of carbon deposited on nickel foils and nickel-alumina catalysts by steam, carbon dioxide and hydrogen in the temperature range 450°–850°C. Carbon deposition was effected by passing a mixture of n-hexane (13.5 molar %), hydrogen (25%) and nitrogen (61.5%) over the catalyst at 600°C. Steam was the most effective gasifying agent at atmospheric pressure. Hydrogen was more effective than carbon dioxide between 500° and 650°C, but the reverse was true at higher or lower temperatures.

Work of this kind may point the way to the regeneration of catalysts deactivated by carbon deposition, though in the particular case just cited it is unknown to what extent the catalyst would be effective for methanation after carbon removal.

Most of the recent catalytic methanation research is concerned with these problems, mostly with nickel catalysts, although not to the exclusion of other materials, notably other Group VIII metals. The aims of the research fall broadly into the categories: maintenance of catalyst activity over long periods, resistance to poisoning and improved techniques of catalyst preparation. Attention is being directed also to the mechanism of catalytic methanation and to the assessment of the specific activity of catalysts.

Methanation catalysis has been reviewed fairly recently by Mills and Steffgen (1973), by Vannice (1976a), by Cusumano and others (1976) and by Ponec (1978). Their excellent and comprehensive treatises have been drawn upon freely in the preparation of this paper, which attempts a review of literature since they appeared.

Also of much interest, although for the most part not dealing specifically with methanation, are papers describing the preparation and testing of a number of catalysts, which were presented at an international symposium in 1975, the proceedings of which were published under the editorship of Delmon, Jacobs and Poncelet (1976).

The approach to catalyst choice and preparation is still much a matter of trial and error and often does not follow strictly scientific principles. The increasing amount of literature in the field is evidence of the truth of the statement in the paper by Mills and Steffgen that "further improvement in methanation catalysts constitutes one of the most fertile fields of research".

2. Methanation in the production of SNG

2.1 Nickel

As already stated, nickel is pre-eminent as a methanation catalyst: it can be very reactive, is selective towards methane production in the reaction between carbon monoxide and hydrogen, and is relatively cheap. Nickel with carbon monoxide can form Ni_3C (Bousquet and others 1972), $Ni(CO)_4$ (Tabij 1975) or even free carbon, but these can be avoided by the correct reaction conditions (Staege and Goeke 1975, White and others 1975, Mohnot and Kyle 1978).

Broadly, Raney nickel or a supported nickel catalyst, or a nickel alloy is used in the temperature range 250°–450°C and under pressures of 3000 to 6000 kPa (Vannice 1976a). Most commercial nickel catalysts consist of 25–77% nickel dispersed on a refractory support of high surface area such as alumina or kieselguhr. Often commercial preparations are used in the form of cylindrical tablets, perhaps 9.5 x 9.5 mm or 6.5 x 6.5 mm in size (Franz and Hess 1973). Suitable catalysts also include such materials as NiO-MgO precipitated on kaolin and reduced in hydrogen (Franz and Hess 1973) or nickel, ThO_2, MgO and kieselguhr.

The composition of a number of nickel methanation catalysts as summarised by Mills and Steffgen (1973) is shown in Table 3. Vannice (1976b) has compared the specific activity of nickel catalysts from various studies by expressing the results on a comparable basis, i.e. after adjustment to the same hydrogen and carbon monoxide pressure and expressed at the same temperature. His comparison is shown in Table 4. For the data from which the figures in this table were derived the Reader is referred to Table 7b in Vannice's review (1976a) already referred to. Also of interest at this stage is Table 5, due to Vannice (1976b), showing the rates of reaction between hydrogen and carbon monoxide over nickel catalysts.

2.1.1 Raney nickel

Raney nickel has long been recognised as an effective methanation catalyst. Flame-sprayed Raney nickel alloy catalysts on tube-wall reactors are very reactive (Haines and others 1972, Cusumano and others 1976 p.473), and the good heat exchange properties inherent in such systems aid temperature control of the highly exothermic methanation reaction, but the catalyst, like other nickel catalysts, is very sensitive to sulphur poisoning.

Massive inserts of Raney nickel catalysts to provide a heat sink and thus control reaction temperature are described for use in tube-wall reactors in US patent applications (O'Hare and others 1976, 1977). The inserts were removable and were massive enough to allow the surface to be sand blasted and reactivated with sodium hydroxide solution. The catalysts were made from Ni-Al Raney alloys by leaching with alkali to leave Raney Ni, the remainder of the massive material being unactivated.

A stainless steel X-shaped insert coated with Raney nickel catalyst was used in pilot plant studies of the non-adiabatic methanation reaction (Schehl and others 1976). In preparing the catalyst the stainless steel surface was blasted with iron-free grit and a coating of bonding material, consisting of 80% Ni and 20% Al, was deposited on it to a depth of about 0.18 mm. Raney nickel alloy powder was then deposited thermally on to the bond surface to a thickness of 0.58mm. Two methods were used for depositing the Raney nickel on the substrate: (i) by flame-spraying with an oxy-hydrogen flame; (ii) by means of a plasma arc with nitrogen as carrier gas. The flame-sprayed catalyst had longer stability.

Table 3 Composition of nickel methanation catalysts *(Mills and Steffgen 1973)*

	Type	Composition	Proportions	Comments	References
1	Alloy	Ni-Al	–	Fluid bed used. Catalyst prepared by partially leaching Ni-Al alloy. Catalyst very active.	Gudkov and Chernyshev 1955 Chernyshev and Gudkov 1956, Bienstock and others 1961, Dirksen and Linden 1963
2		Ni-Al (Raney)	42:58		
3		Ni-Al-Al_2O_3	30-35 Ni: 5-18 Al: 50-60 $Al_2O_3.3H_2O$	Leached Raney Ni catalyst	Rehmat and Randhava 1970
4		Ni-Cu	<4% Cu	CH_4 yield reduced if catalyst contained >4% Cu	Cratty and Russell 1958
5		Ni-M-Al	10 : 2 : 1		Wendlandt and others 1954, Wendlandt and Hoffman 1958
6	Ni compound	2NiO Al_2O_3. 4.7H_2O		Ni hydroaluminate dehydrated in vacuo at 500°C; treated in H_2 at 500°C. Surface area 203m^2/g. Initial reaction rate over catalyst $r_1 = kp_{H_2}^{1.4} p_{CO}^{0.9}$ Rate changed with time and presence of CH_4 to $r = k^{11} p_{H_2}^{0.5} p_{CO}^{1.5} p_{CH_4}^{-0.5}$	Bousquet and Teichner 1972
7		Ni_2B		Precipitated on silica gel from $NiCl_2$	Kurita and Tsutsumi 1961
8	Alumina-supported	Ni-Al_2O_3	23% Ni		Vahala 1971b, Wenke 1958
9		Ni-η-Al_2O_3	12% Ni	Reduction at 420°C. (See also note below)	Schoubye 1970
10		Ni-Ca aluminate on β-Al_2O_3 hydrate	27:25:48	A blend of powdered nickel oxide, calcium aluminate and alumina hydrate was water-sprayed and rolled to form pellets, which were calcined to a highly active catalyst. A catalyst of Catalyst and Chemicals inc.	Catalyst and Chemicals Inc. 1970 Catalyst and Chemicals Inc. 1970
11		Ni-K_2O-η-Al_2O_3	11.5:2.5:86	Reduction at 450°C. (See also note below)	Schoubye 1970
12		NiO-MgO-Al_2O_3	20:55:25	Reduction at >600°C (see also note below)	Schoubye 1970
13		Ni-Mn on Al_2O_3 and diatomaceous earth	100:20:350:100	Prepared by co-precipitation of nitrates with alkali in presence of diatomaceous earth, filtering and washing. Filter cake produced was extruded and dried and activated in H_2 for 2h at 340°C or for shorter time at 400°C.	Novohradsky 1960
14	Spinel-supported	NiO-$MgAl_2O_4$	9–10% Ni	Reduction at 420°C. (see also note below)	Schoubye 1970
15		NiO-K_2O-$MgAl_2O_4$	9-10% Ni; 2-3% K_2O	Reduction at 570°C. (see also note below)	Schoubye 1970

	Type	Composition	Proportions	Comments	References
16	Chromia-supported	NiO-Cr_2O_3	4.2:1 (mol)	Reduction at 300°C. Catalyst had apparent activation energy 86kJ with CO_2.	Solo 1962
17		Ni-Cr_2O_3		A cheap iron catalyst is used in the first stage to remove sulphur poisons and partially methanate the gas. See also Section 3.3.	Schishkova and others 1970, Skol and others 1970
18		Ni-Cr_2O_3	50 : 50	Reduction at 350°C. (See also note (a) below)	Schoubye 1970
19		NiO-Cr_2O_3	1:0; 1.8:4 and 9.0:1	Ni on Cr_2O_3 less active than Ni on kieselguhr	Vahala 1971a, Vahala and Jademik 1971
20		Ni-Cr_2O_3	23% Ni	See catalyst 8 above.	Vahala 1971b
21	Kieselguhr-supported	Ni-ksr	59% Ni	CH_4 and CO from CO_2	Dew and others 1955
22		Ni-ksr		Comparable to Raney Ni	Dirksen and Linden 1963
23		Ni-ksr	58% Ni	Section 3.1.	Randhava and others 1969b
24		Ni-ksr	23% Ni	Compares favourably with other compositions	Vahala 1971b
25		Ni-MgO-ksr		Organic S compounds removed in first stage by use of sulphided Ni	Ruhrchemie A.G. 1957
26		Ni-MgO-ksr	60:5:35	Methanation reaction maintained at 165°C – 205°C. Gas rates up to $5000h^{-1}$ space velocity	Rottig and Schenk 1955
27		Ni-MgO-ksr	60:10:30	Methanates >15% CO_2 at 150° – 250°C in two stages to give yield of 98–99%.	Rottig 1962

There emerged the following observations concerning catalyst composition:

1. There was an effect of carrier on methanation rate in which ηAl_2O_3, Cr_2O_3 > $MgAl_2O_4$
2. Apparent activation energies varied from 75 to 117kJ/mole with the lowest value assigned to η-Al_2O_3
3. Both K_2O and MgO promoters had an adverse effect on methanation activity; K_2O was particularly harmful
4. Regarding catalyst 4 it is of interest that the addition of copper to nickel reduces the activity of nickel and reduces its selectivity towards methane formation (Araki and Ponec 1976, Van Barneveld and Ponec 1978).

Table 4. Comparison of specific activities of nickel catalysts *(Vannice 1976b)*

For reaction $3H_2$ + 1 CO at pressure 103 kPa

Catalysts	Temp. (°C)	N_{CH_4} x10^3 (s^{-1})	Ni Crystallite size (nm)$^{(a)}$	Dispersion$^{(b)}$ (%)	N_{CO}x10^3 (s^{-1})	References
5%Ni/Al_2O_3	275	37	9.0	11	44	Vannice 1975a, b
15%Ni/Al_2O_3	275	35	–	–	43	Bartholomew 1975
Ni/Al_2O_3	275	35- 75	8.5	12		Bousquet & Teichner 1972, Bousquet and others 1972
Raney Ni	275	45	32.0	3.1	115	Dalla Betta and others 1975
8.8% Ni/Al_2O_3	275	85	38.5	2.5	128	Vannice 1976b
3%Ni/Al_2O_3	275	99	12.0	8.4	119	Bartholomew 1975
2%Ni/Al_2O_3	275	90	30.0	3.3	220	Dalla Betta and Others 1975
5%Ni/Al_2O_3	275	91	12.5	7.9	170	Dalla Betta and others 1974
16.7% Ni/ SiO_2	212	1.7	13.0	7.7	–	Vannice 1976b
12.2%Ni/ SiO_2	212	0.61	6.5^c	10.0^d	–	Fontaine 1973
5.3%Ni/ SiO_2	212	0.56	5.5^c	11.8^d	–	Fontaine 1973
2.0%Ni/ SiO_2	212	0.29	4.5^c	14.6^d	–	Fontaine 1973

N_{CH_4} : Turnover number for methane as molecules of CH_4 formed per second per metal site.

N_{CO} : Similarly for carbon monoxide.

a : Calculated assuming spherical Ni particles

b : Represented as H/Ni ratios.

c : Estimated from CO desorption assuming a 1:1 ratio between linear and bridged CO.

d : Expressed as CO/Ni ratios.

Table 5. Rates for reaction between hydrogen and carbon monoxide at 275°C (H_2/CO = 3) *(Vannice 1976b)*

Catalyst	Rate/g Ni CH_4 (CH_4/s)	E_{CH_4} (kJ/mol)
5% Ni/ηAl_2O_3	70	98
8.5%Ni/ηAl_2O_3	37	110
42%Ni/α Al_2O_3	13	154
30%Ni/αAl_2O_3	36	123
16.7%Ni/SiO_2	9.8	111
20%Ni/graphite	27	147
NiO (reduced)	1.0	103

Flame-spraying aluminium onto a nickel surface was used by Baird and Steffgen (1977) in the preparation of methanation catalysts. The sprayed surfaces were heated at various temperatures from 400° to 950°C to form Raney-type alloys and activated by leaching with alkali. It was observed that at 400°C little alloying occurred even when the surface was heated for over 900h. Alloy formation was rapid near or above the melting point of aluminium, and the most active methanation catalyst was made with an alloying temperature of 725°C. The investigators concluded that active catalysts were not made by slow diffusion of one metal into the other at methanation temperatures.

This conclusion is of interest in relation to two other patent specifications describing processes depending on intermetallic diffusion. In one (Larson and Snape 1974) a layer of nickel and one of aluminium are electrodeposited on a metallic surface, which is then heated to 480°C (i.e. well below the fusion temperature of aluminium) for some hours to enable, it is stated, the aluminium to diffuse into the nickel layer. Aluminium is subsequently removed by leaching with 25% NaOH at 90°C. In the other specification (Sanker and others 1976) much higher temperatures are used and very short times allowed for diffusion. Molten aluminium heated to about 850°C is cast round a nickel substrate in a mould at about 1050°C. The metals are retained in the mould at this temperature for only about 30 s and allowed to cool. The casting is activated by leaching with hot sodium hydroxide solution. Raney nickel catalysts made in this way can have layers about 1.3 mm thick on both sides of the subtrate.

Raney nickel catalysts have also been prepared by dip-coating nickel sheets in molten Ni-Al alloy; coatings are formed at 1050°C (Oden and others 1976). The coated material is heated-treated and quenched at 700°C in molten $CaCl_2$–NaCl. The catalyst is prepared by leaching out aluminium with sodium hydroxide solution. Partially coating a heat-conducting support with a catalyst in this way provides a means of controlling an exorthermic reaction, since the heat generated can be removed by conduction and convection (Russell and others 1977).

A method of removing reaction heat adopted by the Pittsburgh Energy Technology Center involves the use of an adiabatic hot-gas recycle methanator. The catalyst comprises Raney nickel flame-spray coated onto a stainless steel grid of parallel plates. In this system, gas containing 75% H_2 and 24% CO was methanated at 2170kPa, at temperatures up to 475°C and at space velocities up to 300 h^{-1}. The product gas contained <0.1%–4% of CO, and 900m^3 of CH_4 were produced during 2307 h of operation (Haines and others 1972, 1974). The Center found that their Raney nickel catalyst had greater activity and longer life than a precipitated nickel methanation catalyst. This observation was in line with that of Dalla Betta and others (1975), who found that under steady state conditions a Raney nickel catalyst was more active than nickel supported on Al_2O_3 or ZrO_2. See Table 4.

In an analogous device a methanator comprises metal tubes metallurgically coated on the inside with Raney nickel catalyst (Fukui and others 1976). Reaction gas flows through the tubes in contact with catalyst while cooling medium is passed over the tubes to remove reaction heat.

A Japanese patent specification describes the formation of a catalyst layer on the surface of an alloy of high strength and ductility having latent catalytic properties (i.e. one containing Ni or Co) (Fukui and others 1977). For example, aluminium was diffused by powder packing into the surface of a treated alloy containing

Ni	35.03%
Cr	24.87
Mn	1.51
Si	1.48
C	0.41
Fe	balance

Diffused aluminium was leached out with 20% NaOH at 80°C.

Removal of reaction heat can also be accomplished by the use of a Raney nickel catalyst in aqueous phase. It has been claimed that with such a catalyst containing platinum group metals, and with the addition of 158,760 kg/h of water, methane containing CO 0.1, CO_2 0.1, H_2 2, N_2 7% could be made at 184–194°C and 2010-2155 kPa from a fuel gas of composition:

CO	25.0%
CO_2	25.0
CH_4	10.0
H_2	35.0
N_2	5.0

at a rate of 208, 150m^3/h (Harris and Fowler 1975).

An investigation has been made into the effectiveness for CO hydrogenation of Raney nickel catalysts prepared from precursors in the range of compositions $NiAl_3$ to Ni_2Al_3 at 300°–360°C. It was found that the catalyst from the percursor Ni_2Al_3 was such less active in methanation than the other catalysts (Oden and Russell 1978).

2.1.2 Nickel-alumina

Cobalt, copper, iron, zinc oxide, barium oxide, calcium oxide, magnesia, chromia, alumina were investigated as promoters for nickel in the catalytic methanation of carbon dioxide (Barcicki and others 1977). Experiments were made with layers of catalyst on a quartz surface. It was observed that with respect to activity and thermal stability alumina, chromia and magnesia were the best promoters. It was found also (Kreindel and others 1974) that from the standpoint of thermal and mechanical stability the best of a number of NiO methanation catalysts on supports of Al_2O_3, a mixture of Al_2O_3 and CaO, MgO, SiO_2 and Cr_2O_3 was NiO-Al_2O_3 containing 35% NiO.

Dalla Betta and others (1975) in a paper referred to in Table 4 describe investigations into the reaction between hydrogen and carbon monoxide over Ni-Al_2O_3 (2%Ni), Ni-ZrO_2 (5%Ni) and Raney Ni catalysts. The supported catalysts were prepared by impregnation into alumina or zirconia. Initially the activity was similar for the three catalysts. Under steady state conditions activities were lower and in the order Raney Ni> Ni-Al_2O_3> $NiZrO_2$. The large decrease in activity under steady state conditions was temperature dependent. There was a large decrease in activity when sulphur compounds even in low concentration were added to the reaction stream. Sulphur impaired the ability of the catalyst surface to hydrogenate carbon atoms more severely than the ability to form C-C bonds, i.e. the formation of hydrocarbons higher than methane began with the addition of sulphur to the reactants.

In addition to the publications cited in Tables 3, 4 and 5 nickel-alumina catalysts have been described in a number of recent patent specifications. Thus, a German patent (Fremery and others 1976) was granted for a process in which a mixture of:

H_2	64.7%
CO	15.2
CO_2	17.9
CH_4	2.2

was converted by a Ni-Al_2O_3 catalyst at 550°C and 3000 kPa to a product comprising :

H_2	22.8%
CO	1.1
CO_2	32.2
CH_4	43.9

A catalyst comprising:

NiO	10.0%
Al_2O_3	89.6
$SiO_2-Fe_2O_3$	0.1
K_2O	0.3

when used for the methanation of hydrogen and carbon monoxide at 3000-4500kPa in which the materials passing over the catalyst rose in temperature from 350°–450°C to 510°–615°C, was claimed to show no loss of catalyst activity after 800 to 1000 h (Fremery and others 1978).

A simple co-precipitated Ni-Al_2O_3 catalyst is used in a process, the subject of a US patent (Thompson 1971), in which conversion of liquid hydrocarbons to SNG is effected in two stages: steam reforming followed by methanation. Catalysts of co-precipitated Ni-Al_2O_3 (containing 50% Ni) with 3% graphite and Ni-keselguhr (containing 50% Ni) with 3% graphite were also used in a two stage process for the methanation of synthesis gas (Hansberger and Hammons 1977).

It is perhaps of interest to note that although under normal conditions in the hydrogenation of carbon monoxide nickel alumina catalysts are very selective towards methane formation, co-precipitated nickel alumina catalysts, if reduced at low temperature, can give rise to products containing higher hydrocarbons (Doesburg and others 1977).

A US patent application (Tabjl 1975) claims the prevention of $Ni(CO)_4$ formation and catalyst damage by methanation over a Ni-Al_2O_3 catalyst in multiple stages. Multi-stage methanation of H_2 and CO over an alkali-promoted Ni-Al_2O_3 catalyst is referred to in a Canadian patent specification (Galstaun 1977) and over a Ni-Al_2O_3 catalyst in a Japanese patent (Imperial Chemical Industries Ltd. 1976). Another multi-stage process (White and Roszknowski 1976) used Ni in low proportion on a thermally stabilized ceramic alumina base, such as is usually employed in the steam-reforming of methane to hydrogen and carbon monoxide. It was claimed that catalysts of low Ni content are less sensitive to steam and are stable at higher temperature than catalysts of high Ni content.

Other methanation catalysts of low metallic content have been formulated to contain nickel promoted with cobalt. One of these (Parthasarathy 1976) comprises NiO and CoO in a Ni/Co ratio of 1:1.5 supported on very pure γ Al_2O_3. The catalyst was made by impregnating the alumina with a solution of nickel and cobalt salts, heating the resulting mass at 300° to 500°C, and reducing in hydrogen at 250° to 600°C. The catalyst had a surface area of 100 to 200 m^2/g, with a pore volume of 0.25 to 0.7m^3/Mg. The metal content was 3 to 10%.

A catalyst of rather similar formulation contained Ni and Co on a refractory support (e.g. Al_2O_3), free of alkali, having a surface area of at least 1 m^2/g. The Co content of the catalyst was at least 0.5% and the Ni content 5 to 70%. The formulation was said to reduce carbon deposition in methanation reactions (Kang 1976).

A bimetallic catalyst of nickel and cobalt not supported on alumina was prepared in the following way. A 10% solution of oxalic acid was added to a slurry of Ni and Co carbonates until a constant pH of 2 was reached. The residue from the resultant slurry was reduced in hydrogen at 360°C for 3 h and then cooled in CO_2 (Bland 1975).

A catalyst with a specific surface 5–200 m^2/g consisting of 2-20% Ni and Co supported on amorphous alumino silicate (Al_2O_3 5–35%) was prepared by impregnating the support with nickel and cobalt nitrates and firing (Grace 1976). The catalyst was reduced in hydrogen. With the catalyst a gas mixture containing:

CO	20.0%
H_2	58.0
CO_2	2.0
CH_4	2.0

underwent above 80% methanation at 400°C at 7000 kPa.

A thermally stable Ni-Al_2O_3 methanation catalyst is prepared, it is claimed by a technique involving the dispersion of alumina hydrate as boehmite in an aqueous solution of an ammino complex of a nickel salt (McArthur 1977b, 1977c). The slurry is heated to effect gradual decomposition of the ammino complex with precipitation of nickel hydroxide in the pores of the alumina hydrate. This product is filtered, heated and extruded or tabletted. The tablets are calcined to convert the alumina hydrate to γ-alumina, and contain 40-65% NiO and 35-60% Al_2O_3. The material can be reduced in hydrogen.

Broecker and co-workers (1974c) described a Ni-Al_2O_3 methanation catalyst prepared by precipitation of $Ni_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ on Al_2O_3, followed by calcination and reduction in hydrogen. Gas containing:

CH_4	60.5%
H_2	25.4
CO_2	12.5
CO	1.1

was converted to:

CH_4	85.5%
H_2	4.3
CO	10.2

by the catalyst at 1760 kPa and 270°–295°C.

It has been claimed (Dalla Betta and others 1976) that methanation catalysts of nickel supported on zirconia are resistant to poisoning by sulphur compounds, and there is other evidence that zirconia in a nickel catalyst support increases catalyst life, although it may reduce activity. A German patent (Anderson and others 1976) claims durability and stability in hydrogen and steam for a catalyst of nickel supported on Al_2O_3/ZrO_2. The life of a similar catalyst (an Al_2O_3/ZrO_2 support containing 32% Ni) is reported to be much increased by the addition of 0.25 - 8% molybdenum, though at the cost of a slight decrease in initial activity (Topsoe 1976).

Metal sponges for supporting or compromising catalysts have been described (Golebiowski and others 1977 b, c, d, Instytut Nawozow Sztucznych 1977). Their principle use is to remove heat from exothermic reactions and aid in controlling the temperature. Thus, catalyst tubes for steam-reforming of hydrocarbons and methanation have been made by electrochemical deposition of nickel sponge on the inner walls. After scouring of the nickel deposit the tubes were roasted with aluminium nitrate and then with nickel nitrate to form alumina and a nickel catalyst. In a typical preparation the catalyst, containing 6% Al_2O_3, had an internal surface of 12 m^2/g (Golebiowski and others 1977a).

Catalysts stated to be more active than those prepared by conventional methods were made by introducing nickel into alumina through the controlled adsorption of $Ni(CO)_4$. Catalysts produced had a specific nickel surface of 2-15 m^2/g (Dergachev and others 1972, 1973).

An unconventional technique was used to produce nickel-alumina catalysts claimed to be thermally very stable (Hansford 1976). An aqueous solution of $Ni(NO_3)_2$, $Al(NO_3)_3$ and urea was heated to a temperature at which the urea was hydrolysed to CO_2 +NH_3, delayed co-precipitation from the nitrates ensuing. The co-precipitate was washed, dried, shaped and calcined. The catalyst was active, although the surface area of the active metal was low (generally below 18 m^2/g) even for catalysts containing 60% of active metal oxide.

The patent specification covers similar formulations using iron, cobalt or copper as well as nickel.

2.1.3 Nickel-chromia

It has often been reported that better methanation catalysts can be obtained from nickel-alumina than from nickel-chromia formulations. For example, Kreindel and others (1974) in studying NiO catalysts on Al_2O_3, Al_2O_3-CaO, MgO, SiO_2 and Cr_2O_3 found that a NiO-Al_2O_3 catalyst containing 35% NiO was the best from the stand point of thermal and chemical stability. And in a patent specification claiming good performance and thermal stability for methanation catalysts consisting of 25-45% NiO and 0.1-0.3% CuO and porous Al_2O_3-SiO_2, it was stated that a catalyst comprising 61.9% NiO and 38.1% Cr_2O_3 performed well initially but had poor thermal stability and low activity after heat treatment (Luft and others 1975). Despite this, however, several nickel-chromia catalysts have been described recently, some of which are referred to in the tables and in the section on methanation for gas purification.

A so-called nickel-chromite methanation catalyst was prepared by co-precipitation from an aqueous solution of nickel nitrate and a hexavalent chromium compound using ammonia. The finely divided precipitate was calcined to produce material containing a limited amount of hexavalent chromium, which was then reduced to trivalent chromium without reduction of nickel oxide (Stiles 1976).

Another patent specification describes the preparation of a nickel-chromia catalyst from a solution containing $Ni(NO_3)_2$ and $Cr(NO_3)_3$ (Jelink and others 1969). Although primarily for the selective hydrogenation of aldehydes, the catalyst was satisfactory for the methanation of oxides of carbon.

A catalyst comprising 30–50% Al_2O_3, 50-60% NiO, 3-10% Cr_2O_3 and 3-10% MgO was prepared by the calcination of precipitates of Al_2O_3 (from $Al(NO_3)_3$), NiO (by boiling Ni complexes), CrO_3 (from $Cr(NO_3)_3$) and MgO (Cobzaru and others 1971).

2.1.4 Nickel-magnesium compounds

Simple nickel-magnesium catalysts have been prepared by the co-precipitation of nickel and magnesium carbonates followed by heating for 6-8 h at 300°–500°C (D'Yakonov 1971).

A German patent describes the preparation of a methanation catalyst precursor by depositing precipitated nickel carbonate on a magnesium silicate carrier. Catalysts were prepared from this material, after drying to granulate it, by mixing with boehmite, hydrargillite or Al_2O_3 (Sapper and Laurer 1978).

A group of methanation catalysts, claimed to be superior to nickel precipitated on kieselguhr or alumina in respect of thermal stability and carbon deposition (Kobylinski and Swift 1977, Robinson 1973), comprised magnesium substituted nickel chrysotiles, i.e. layered complex metal silicates having repeated units of formula $[(1\text{-}x)\ Ni^{2+} + x\ Mg^{+2}]_3\ (OH)_4\ Si_2O_5\ w\ H_2O$, where x = 0.01 to 0.6 and w = 0 to 4.

Typical catalyst compositions were represented by $(Ni_{0.83}\ MgO_{0.16})_3\ (OH)_4\ Si_2O_5.w\ H_2O$, with surface areas, as determined by the Brunauer, Emmett, Teller (B.E.T.) method, ranging from 100 m^2/g to 150 m^2/g.

Akin to this substituted chrysotile as a methanation catalyst is unsubstituted nickel chrysotile, $Ni_3OH_4Si_2O_5$. This was prepared from colloidal silica and nickel chloride. It was effective for methanation between 200° and 600°C, and was claimed to be a better catalyst than nickel supported on silica mainly because of its longer life and better selectively towards methane formation and because it is less conducive to the formation of carbon on the catalyst (Kobylinski and Swift 1976).

Inclusion of kaolin in $Ni\text{-}Mg\text{-}Na/Al_2O_3$ gave catalysts claimed to be stable and strong for over 980 h at 650° and over 1500 h at 525°C. The material was specified for use in two-stage methanation of synthesis gas (Gent and others 1975).

Broecker and others (1976) described methanation catalysts of good stability prepared by the precipitation of $Ni_5Mg\ Al_2O_9$ on titania, zirconia or alumina, followed after calcination by treatment with Ca aluminate and reduction. These authors, incidentally, have specified $Ni_5Mg\ Al_2(OH)_{16}\ CO_3.4H_2O$ as a precursor in the preparation of a catalyst for producing methane by the steam reforming of hydrocarbons (Broecker and others 1974a, b). The sintering of catalysts in which $\gamma\text{-}Al_2O_3$ is converted to $\alpha\text{-}Al_2O_3$ is hindered by compounds of this kind because MgO and Al_2O_3 can react to form spinel; in the formation of this the average pore radius is increased (Kaempfer 1975).

A catalyst precursor containing $Ni_6Al_2(OH)_{16}.CO_3.4H_2O$ and $Ni_{15}MgAl_2(OH)_{16}\ CO_3.4H_2O$ has been prepared by treating nickel nitrate, magnesium nitrate and aluminium nitrate with Na_2CO_3 and adding $Al_2O_3.3H_2O$ and heating. Methanation catalysts were obtained by heating the precursor, mixing with a carrier and tabletting (Woodward 1975).

Nickel methanation catalysts containing magnesium have also been prepared by adding an aqueous solution of $NaBH_4$ and Na_2CO_3 to a solution in methanol of nickel nitrate and magnesium nitrate cooled to O°C (Hammer and Ibrahim 1976; Hammer and Hakim 1978). The precipitate was reduced in hydrogen at a temperature about that required for methanation. The role of the boride is not altogether clear, but the specification covering the formulation includes also catalysts made as above but with aluminium nitrate replacing magnesium nitrate: in the latter case B_2O_3 derived from the borate may increase stability of the catalyst by inhibiting the formation of $\alpha\text{-}Al_2O_3$ (Cusumano and others 1976, p33).

The beneficial effect of including MgO in nickel catalysts for hydrogen purification is referred to in Section 3.1.

2.1.5 Nickel with rare earth elements

Methanation catalysts consisting of nickel with rare earth elements have been investigated. Atkinson and Nicks (1977) worked with alloys of nickel and mischmetal (Ce67, La13, Pr9, Nd11%) in various proportions and compared the catalyst made from these with a commercial catalyst containing 15% Ni on Al_2O_3. They found that the mischmetal samples were more active than the commercial catalyst, the most active being that containing 30% mischmetal: their results are summarised in Table 6 below.

Atkinson and Nicks (1976) have applied for patent cover for methanation catalysts composed of an oxide of a rare earth metal with a Group VIII metal or its carbide. The specification describes *inter alia* catalysts prepared from precursors of alloys of approximate compositions $CeNi_5$ and $CeCo_5$. Alloys of approximate compositions $CeNi_2$ and $CeCo_2$ have also been described as precursors for methanation catalysts (Luengo and others 1977).

Table 6. Activity of mischmetal catalysts
(Atkinson and Nicks 1977)

Catalyst	Surface area (B.E.T.) m^2/g	CO uptake on catalyst μmole/g	E kcal/mol	Turnover number at 275° C x 10^3 (molecules CH_4 formed per active site of catalyst per s)
commercial (15% Ni/Al_2O_3)	77.6	177	27	13
20%m*-Ni	20.1	87	28	65
30%m-Ni	30.0	286	32	150
40%m-Ni	35.0	313	32	111
50%m-Ni	37.2	172	31	728

* m= mischmetal

However, although interesting, catalysts of this kind are unlikely to be favoured just for methanation. Under reaction conditions they decompose into a rare earth metal oxide or oxides and free cobalt or nickel, and in their decomposed state they are not more reactive than free cobalt or nickel. Moreover, they tend to be less selective towards methane formation, as against higher hydrocarbons, than free cobalt or nickel, particularly the latter (Luengo and others 1977, Wallace and others 1977).

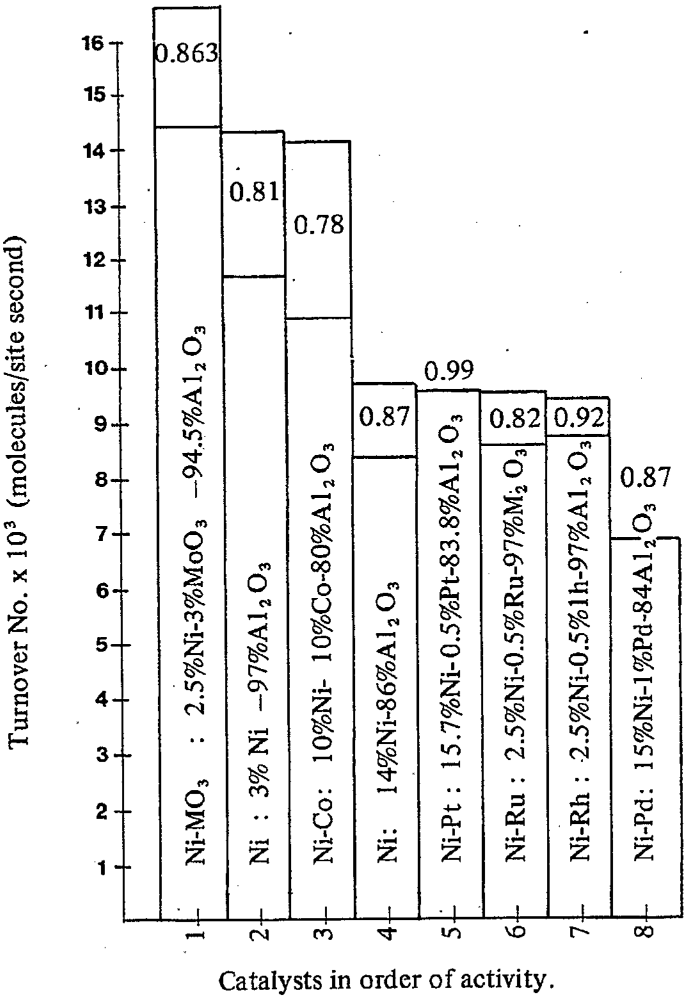
It is stated in a Japanese patent that a methanation catalyst prepared by heating $Ce(OH)_4$ at 700° C exhibits some resistance to poisoning by H_2S (Tomii and Kaneko 1976).

A catalyst efficient for the methanation of oxides of carbon consisted of small amounts of La_2O_3 and Ru incorporated with a nickel substrate supported on silica. The activity of the Ni-La_2O_3-Ru catalyst was much greater than that of the components. Whereas over a nickel catalyst the rate of CO methanation was greater than that of CO_2, the opposite was true over both the Ni-La_2O_3-Ru catalyst and a Ru catalyst (Inui and Funabiki 1978, Inui and others 1978).

2.1.6 Nickel alloy catalysts

References are made in this review to bimetallic or alloy catalysts, but the literature in this field is not extensive. Bartholomew and Barton (1976) have studied alumina-supported alloys of nickel with ruthenium, rhodium, molybdenum oxide, iron, cobalt, platinum, palladium and copper as methanation catalysts. Reactant gases comprise 1% CO, 4% H_2 and 95% N_2 were used for determining activity data under conditions such that effects of heat and mass transfer were minimized; specific rates were reported at 1 bar and 225° and 250°C, based upon active surface areas. Catalysts were prepared by co-impregnation of the alumina support, followed by drying and reduction in a stream of hydrogen at space velocity 1000-2000 h^{-1} while heating at less than 5° C/minute to 450-500°C.

Bartholomew and Barton found that turnover numbers were not significantly different for Ni-Rh, Ni-Ru and Ni catalysts and compare favourably with initial rates reported for 5%Ni/Al_2O_3 and 0.5% Ru/Al_2O_3. Ni-MoO_3/Al_2O_3 was the most active catalyst on a surface area basis and a 14% Ni/Al_2O_3 the most active on a mass basis. Ni-Pt/Al_2O_3 had the highest selectivity towards methane production. Their results are typified in Fig. 1.



Reaction conditions: Temp.: 250°C

Space velocity: 30,000h

Fractions represent selectivity to methane production.

Figure 1. Turnover Numbers (molecules product/site sec) for Methanation on Nickel and Nickel Alloy Catalysts (Bartolomew and Barton 1976)

2.1.7 Other nickel catalysts

Several other nickel catalysts have been described as follows:

1. Nickel and promoter supported on calcium phosphate:
   In the preparation of this methanation catalyst, calcium phosphate, precipitated from aqueous solutions of a calcium compound and a phosphate, was compounded with suitable nickel and promoter metal compounds. After drying the mixture was tabletted and before use reduced with hydrogen at 300°C to 650°C, with or without prior calcination. Barium or uranium was used as promoter. Typical preparations contained Ca,P,Ni and Ba or U in the proportions 5-35, 2-20, 10-50 and 1-20 or 2-40% (Johnson and others 1977).

2. Intermetallic compounds:
   Intermetallic compounds of formulae $ThNi_5$, UNi_5, $ZrNi_5$ were found to be effective methanation catalysts (Elattar and others 1977). These materials are similar to the compounds $CeNi_5$ and $CeNi_2$ referred to in the section on nickel and the rare earth compounds (Section 2.1.5), and like those decompose under reaction conditions, so that in use $ThNi_5$ is transformed into Ni supported on ThO_2 and $ZrNi_5$ into Ni supported on ZrO_2. Auger spectroscopy indicates that in the latter case the nickel is overlaid with graphite, but this does not occur with the nickel on ThO_2 (Moldovan and others 1978). This accounts for the greater activity of Ni on ThO_2 than of Ni on ZrO_2. It has been claimed that methanation catalysts supported on zirconia are resistant to sulphur poisoning (Dalla Betta and others 1976), but $ThNi_5$ has greater resistance to sulphur than $ZrNi_5$ because the transformed $ThNi_5$ has a large surface area of nickel.

   It was stated that the specific activity of $ThNi_5$ is greater than that of a typical commercial oxide-supported catalyst (Elattar and others 1977).

2.2 Cobalt

Cobalt is a very active catalyst for the hydrogenation of oxides of carbon. It is less selective than nickel towards the formation of methane, although that predominates in the hydrocarbon products above 300°C. For example, from catalysts comprising 1-15% CoO, 15-60% Al_2O_3 and 35-70% ZnO, mixtures of hydrocarbons (C_1 to C_4) containing 82-99% CH_4 were obtained from mixtures of hydrogen and carbon monoxide in the proportions (47:53 to 60:40) at 350° to 450°C, 1,400 to 69,000 kPa, with space velocities 500 to 6000 h^{-1}. In preparing the catalysts hydroxides of Co, Al and Zn, separately precipitated with ammonium hydroxide from solutions of nitrates or acetates, were mixed and calcined (Khera 1976).

Raney cobalt has been reported as very active for CO methanation (Bienstock and others 1961).

It is of interest that cobalt catalysts were among the first developed for the production of liquid hydrocarbons from water gas by the Fischer-Tropsch process (Vannice 1976a, Storch and others 1951).

Methanation catalysts containing both nickel and cobalt are referred to in Section 2.1.2.

In general, techniques for the preparation of nickel catalysts can also be applied to cobalt catalysts.

2.3 Iron

Methanation catalysts can be prepared from iron, but nickel is far more effective in yield, activity and selectivity towards methane production (Haynes and others 1972), and reduced, promoted iron oxide is best used as a catalyst in the Fischer-Tropsch synthesis (Storch and others 1951). It may be noted, however, that in terms of unit surface area of active metal iron is intrinscially as active as nickel. Some nitrided iron catalysts are compared with nickel and cobalt catalysts in respect of methanation in Table 7, which quotes results from the work of Haynes, Elliot and Forney (1972).

At slightly elevated pressure (ca. 1000kPa) both cobalt and iron catalysts with CO and H_2 give olefins and alcohols as well as paraffins, but cobalt gives a much lower proportion of olefins and alcohols (Vannice 1976a, Storch and others 1951).

Iron-containing catalysts of the type $M[Fe(CN)_2]$ have been described for the reduction of CO to produce hydrocarbons, especially CH_4, C_2H_4, C_2H_6, C_3H_8. The cation M can be Ce, Cu, Co, Fe, Ni, Mn, Ag, Ca, Mg, or Zn or can be a composite of two or three cations (Vogt and others 1978).

Catalysts consisting of finely divided iron suspended in molten metal salts are referred to in Section 2.8.

2.4 Ruthenium and the 'noble' Group VIII metals

The precious metals of Group VIII are catalytically active for methanation. Ruthenium, in particular, is outstandingly active even at low temperature and under mild hydrogenation conditions, where it is, perhaps, the most active of the methanation catalysts. It is, however, expensive and therefore is normally encountered at low attenuation (0.5% support) at which it is not markedly superior to nickel. Table 8 after Vannice (1976a), compares the specific activity of ruthenium with that of other catalysts. Data for Table 8 were obtained at low conversion in order to minimize heat and mass transfer problems. Vannice concluded that the methanation could be described by a law of the form

$$[rCH_4 = A\ \exp.(-E_m/RT)P_{H_2}{}^{x}.P_{CO}{}^{y}]$$

where the rate, rCH_4, is equal to the turn-over number as defined in the notes to Table 4.

With regard to selectivity towards methane formation (as against hydrocarbons and other materials of higher molecular weight) the picture is, however, different and ruthenium is the least selective of the catalysts listed in Table 8 (Vannice 1975a). It is of interest that at low temperature and high pressure ruthenium induces the production of high molecular weight paraffin wax.

A major disadvantage in the use of ruthenium is its high cost. Despite this, however, ruthenium (and other expensive Group VIII metals) are still investigated as methanation catalysts because of their high activity which makes their use in attenuated form possible.

Kester (1974) and Lunde and Kester (1974) investigated the methantion of carbon dioxide over four catalysts: (i) 80% Ni and NiO on kieselguhr, (ii) 0.5% ruthenium on alumina, (iii) 0.5% rhodium on alumina, (iv) 0.5% cobalt on alumina. In agreement with others, they observed that Ru and Ni were the most active catalysts, Ru being rather more active than Ni. But they reported that Ru presented less operating difficulty than Ni in respect of sulphur poisoning

Table 7. Methanation with catalysts in fixed beds *(Haynes and others 1972)*

Pressure : 2170 kPa

Catalyst composition and pretreatment	H_2/CO ratio	Methanation Conditions space velocity h^{-1} *	Temp. °C	CH_4 in products % vol (CO_2,H_2O free)
Cuban iron ore - - reduced	1	100-300	321	37.5
Fused Fe_3O_4, reduced and nitrided N/Fe = 0.44	2	100-300	395	30.5
Fe_3O_4 (50%) and ball clay, reduced and nitrided N/Fe = 0.48	2	100-300	312	27.5
Fe-Ni-MgO-SiO_2 (58.8:12.4:2.21:0.2) N/Fe = 0.314, reduced and nitrided	1	300	273	39.7
Ni, ThO_2-Cr_2O_3 ppt. on kieselguhr (30.0:7.6:1.6:59.9) – reduced	1	100-300	320	60.8
10% Ni impregnated on steam-treated cracking catalyst base reduced	1	300		insignificant
5% Ni impregnated on cracking catalyst base – reduced	1, 2	300	398	44.6
5% Ni impregnated on cracking catalyst base plus K_2O – reduced	2.5	300	400	39.1
1% Ni impregnated on activated charcoal – reduced	1	100-300		insignificant
10% Ni ppt. on silica – reduced	1	100-300	355	48.3
NiO-Al_2O_3 ppt. on kaolin (100: 200: 125) -- reduced	2	300	300	98.9
NiO-MgO ppt. on kaolin (100: 200: 125) – reduced	2.5	300	264	97.3
28% Ni, 5.5% Mn, 2.4% Al ppt. on kaolin – sintered and reduced	2.5	300		insignificant
NiO, MnO, Al_2O_3 ppt. on cracking catalyst – reduced	2.5	300	404	17.3
Ni pellets steam-treated – reduced	2.5	100-300		insignificant
Raney cobalt (50% Co, 50% Al), Al partly extracted with NaOH	2.5	300-2,800	286	92.1
Raney nickel (42% Ni, 58% Al), steam-treated – reduced	2.5	300		insignificant
Raney nickel (42% Ni, 58% Al), Al partly extracted with NaOH	2.5	300-1,500	300	96.9

* Space velocity = Std volumes feed gas per hour per vol catalyst

Table 8. Specific activities and kinetic behaviour of catalysts in CO hydrogenation

(After Vannice 1976a)

$$N_{CH_4} = A \exp. (-E_{CH_4}/RT)\, P_{H_2}^{x} . P_{CO}^{y}$$

$H_2/CO = 3$. Pressure of $H_2 + CO$: 103 kPa

Catalyst	Reactor temp. °C	E_{CH_4} kJ/mole	x	y	N_{CH_4} at 275°C(a) $s^{-1} \times 10^3$
5% Ru/Al_2O_3	205–230	101	1.6	–0.6	181
15% Fe/Al_2O_3	220–255	89	1.1	–0.1	57
5% Ni/Al_2O_3	230–255	105	0.8	–0.3	37
2% Co/Al_2O_3	225–250	113	1.2	–0.5	20
1% Rh/Al_2O_3	250–280	100	1.0	–0.2	13
2% Pd/Al_2O_3	245–260	82	1.0	0	12
1.75% Pt/Al_2O_3	270–300	70	0.8	0	2.7
2% Ir/Al_2O_3	265–285	71	1.0	0.1	1.0

Note (a) compared at 0.75 $H_2/CO=3$ at total

N_{CH_4} is turnover number (see Table 4)

and carbon deposition at above 350°C. With Ni, too, (unlike Ru) reactor start-up in H_2 was advisable to assure reduction of Ni in its most active form.

The authors made a particular study of the hydrogenation of carbon oxides over a catalyst consisting of 0.5% Ru on alumina pellets and presented a reaction rate equation for the temperature range 200° to 370°C.

The kinetics of the reaction between hydrogen and carbon dioxide over ruthenium catalysts have been considered also by Verostko and Forsythe (1974) and by Quach and Rouleau (1976).

Most of the work with ruthenium is carried out in relation to methanation for gas purification, particularly for the selective removal of carbon monoxide from hydrogen, contaminated with oxides of carbon, to be used for ammonia synthesis, and is considered in the appropriate section. The literature reviewed in this section has more general application.

Ruthenium and alloys of ruthenium and platinum mixed with 5-20% reduced amorphous tungsten oxide have been described as catalysts for the methanation of CO and CO_2 (Fleming and others 1975). Selective methanation of CO in gases containing those carbon oxides occurs particularly at temperatures below 150°C.

A catalyst patented for the steam-reforming of naphtha to CH_4, H_2 and CO, which would probably be very satisfactory for methanation, was prepared by adding saturated aqueous NH_4HCO_3 to a hot solution of $Al(NO_3)_3$, $(AcO)_2$ Zn and $RuCl_3$ (Dick 1973). The precipitate was dried at 120°C and pelletized after the addition of 2% graphite. The material was reduced with hydrogen at 350°C to produce a catalyst which contained about 9% ruthenium and about 54% of Al_2O_3.

A United States patent (Kobylinski 1976) describes the preparation of a catalyst for the production of methane from hydrogen and oxides of carbon which comprises a metal silicate having repeated units of $[(1\text{-}x)\ Ni^{a}+xRu^{b}]_n\ (OH)_4\ Si_2O_5.w\ H_2O$ where x=0 to 1, this expressing the atomic fraction of Ni and Ru,

a is the valence of Ni,
b is the valence of Ru,
n is a number defined by the ratio $6/[a(1\text{-}x)+bx]$,
w ranges from 0 to 4.

It is claimed that with catalysts of this kind coke formation is less likely than with other catalysts, disproportionation of CO to CO_2 is less, and catalyst life is longer than with conventional catalysts.

Other catalysts containing ruthenium with nickel or cobalt comprise the adducts $(Ni_2B)_{10}RhH_{15}$ and $(Co_2B)_{10}\ RhH_6$. These are prepared from $NiCl_2$ or $CoCl_2$ with $RhCl_3$ and $NaBH_4$ (Mitchell and others 1976).

In the description of a catalyst containing 1% Rh, a mixture of $RhCl_3$ and graphite was dried at 110°C for 24 h and then treated with air at 550°C in a tubular reactor (Morita and others 1977). The product from a 3: 1 H_2/CO mixture passed through the reactor at 500°C with a space velocity 1800 h^{-1} contained:

H_2	17.5%
CH_4	74.4
$C_2H_6+C_2H_4$	5.0
CO_2	3.1

Methanation catalysts containing nickel, lanthanum oxide and ruthenium are referred to in Section 2.1.5.

A recent Japanese paper points out that thoria is a more effective promotor for palladium catalysts than silica (Fujimoto and others 1978).

2.5 Molybdenum and tungsten

The virtue of molybdenum and tungsten catalysts for methanation is their resistance to sulphur poisoning; they are, in fact, commonly sulphided before use. However, they are only moderately active, require relatively high reaction temperature and are less selective to methane formation than some other catalysts. Table 9 from a paper by Mills and Steffgen (1973) summarises the properties of some molybdenum catalysts. The sulphided catalyst (last column) appears the most effective for methanation.

Molybdenum disilicide ($MoSi_2$), prepared preferably by direct reaction of the elements heated in vacuo or in a protective atmosphere, can function as a methanation catalyst with some resistance to sulphur, though it is not very active (Slaugh 1976). With such a catalyst a mixture of H_2 and CO in the proportions 3:1 at 500°–600°C and space velocity 600–900h $^{-1}$ underwent a 20% conversion of CO to CH_4, i.e.

$$\left[\frac{\text{mols } CH_4 \text{ in product x 100.}}{\text{mols } CO+CH_4 \text{ in product}}\right]$$

With tungsten disilicide (WSi_2) the same gas mixture under the same conditions underwent only little conversion.

Table 9. Methanation over molybdenum catalysts
(After Mills and Steffgen 1973)
Reaction conditions: $H_2/CO = 3:1$ Pressure: 2100 kPa Temperature: 400°C

Mo in catalyst, %	11.2	38.5	40.6	11.0
Catalyst support	Cracking catalyst	Active carbon	Al_2O_3	Al_2O_3
Method of catalyst preparation	Impregnation	Impregnation	Coprecipitation	Coprecipitation $+H_2S$
H_2–CO conversion %	41.1	67.9	37.5	47.6
Hydrocarbon distribution in products, wt. %				
C_1	79.7	83.6	84.1	93.7
C_2	16.0	13.0	15.6	5.9
$C_3 + C_4$	4.3	4.4	0.3	0.4
C_5 +	–	–	–	Nil

Molybdenum has been used in catalysts in association with other active elements. A patent specification describes a methanation catalyst comprising an oxide catalyst, conventionally supported, of general formula $Ni_a Cu_b Mo_c O_x$, where a, b and c are chosen so that when b=1, a and c are in the range of 1 to 9, preferably in the range 1 to 3, and x is determined by the valencies of the other elements (Alcorn and Cullo 1976). The complex is reduced before or during use.

The complex is prepared by impregnating the support (preferably γ-Al_2O_3) with a molybdenum compound, calcining to produce supported molybdenum oxide, which is itself then impregnated with a mixture of Ni and Cu compounds, and again calcining to produce the supported oxide complex.

Catalysts of nickel molybdate supported on Al_2O_3 and SiO_2-Al_2O_3 have been investigated for methanation. The catalysts were effective, but carbon was rapidly deposited on them (Reddy and others 1978).

Methanation catalysts of nickel with molybdenum supported on Al_2O_3 (15-30%Ni, 2-6%Mo) have also been described (Pop and others 1971). The catalysts were made by treating Al_2O_3 with nickel nitrate and ammonium molybdate and reducing in hydrogen.

The addition of tungsten in small proportions to catalysts containing nickel and the "noble" Group VIII metals has been specified, presumably to increase sulphur resistance, but whether it is effective in this respect is doubtful (Fleming and others 1975, Finch and Ripley 1976, Abidov and Munavarov 1977).

Catalysts consisting of finely divided molybdenum suspended in molten metal salts are referred to in Section 2.8.

2.6 Homogeneous catalysts

As pointed out by Cusumano, Dalla Betta and Levy (1976, p477), homogeneous catalysts could in principle be applied readily to methanation reactions, since reactants and products are gaseous and separation would not present difficulty. It has also been suggested that homogeneous catalysts can be sulphur tolerant although this has not been experimentally proved. Of interest, therefore, is a paper describing hydrogenation of CO to CH_4 catalysed by osmium and iridium cluster compounds (Thomas and others 1976). With $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ methane was selectively produced at 140°C and 2 bar pressure at a rate comparing favourably with that over supported iridium (Vannice 1975a). Substitution of the CO groups by phosphites or phosphines raised the catalytic activity of the cluster but decreased selectivity towards methane formation.

A titanium complex, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, catalyses the conversion of a mixture of hydrogen and carbon monoxide to methane at 150°C or under UV radiation at 25°C. This is of theoretical interest, but is, perhaps, of limited practical significance since the complex is rapidly converted to a catalytically inactive cluster (Huffman and others 1977).

2.7 Intercalation

The forces between the layers of reticulated haxagons of carbon atoms in graphite are weak; because of this certain molecules can penetrate the interlayer spaces and react strongly with the layers, a phenomenon termed "intercalation". The strong interaction changes the properties of the graphite and can enhance its adsorptivity, and some graphite intercalates are catalytically active for some reactions. There is interest in the phenomenon because conceivably it might provide a means of preparing catalysts for the direct gasification of coal or carbon in steam or hydrogen (Cusumano and others 1976, p 507).

More immediately, it has been claimed that methanation catalysts incorporating graphite-intercalated nickel, platinum or palladium are better than conventional catalysts in respect of activity, resistance to sulphur poisoning and life, longer life being due to inhibition by the graphite lattice of crystal growth of the metallic phase (Lalancette 1974, 1975). In preparing the catalysts a salt of the metal is mixed with purified graphite and the mixture heated at 530°C in a stream of chlorine for 3 to 10 days. The resultant intercalated graphite complex is reduced by treatment with an alkali metal compound and diphenyl in an organic solvent such as tetrahydrofuran at -50°C in an inert atmosphere. Excess alkali metal salts are removed with methanol and then water.

2.8 Catalyst supports

The importance of catalyst supports is evident from the many descriptions of catalyst preparation cited in this document and, for example, from Tables 4 and 5. With reference to Table 4, Vannice points out that specific activity is sensitive to catalyst support but the variation is less than an order of magnitude. Catalyst supports are dealt with comprehensively by Cusumano, Dalla Betta and Levy (1976, pp30-49) who consider the subject in terms of the effect of the support on:

(i) The availabile surface area of the catalyst:
Clearly the greater the surface area, the more effective is the catalyst, but this can also lead to changes in the phase properties of a catalyst, which can affect its activity and selectivity.

(ii) Thermal stability:

Loss of catalyst activity can occur through decrease in active surface area due to agglomeration in the active metal, to sintering of the support and to interaction between active metal phase and support, effects particularly likely with highly exothermic reactions such as methanation. In particular, with methanation the sintering of nickel crystals can present a problem, and the interaction of Ni/NiO must be controlled by catalyst preparation and catalyst structure.

(iii) The addition of stabilizing compounds to catalyst systems.

Nickel supported on alumina is, perhaps, the most widely considered catalyst for the hydrogenation of CO to CH_4, so that in the context of methanation alumina as a support is of much interest.

In the preparation of a catalyst by impregnation of a support with a solution containing the active species, the technique of impregnation can affect catalyst properties. An interesting study of impregnation variables for the system NiO/Al_2O_3 was made by Cervello and others (1976), who, using commercial γ -Al_2O_3 and an aqueous solution of $Ni(NO_3)_2$, investigated the effects of time of impregnation, previous state of the alumina, concentration of the impregnating solution and successive impregnations. Nickel cation distribution along the diameter of catalyst pellets was determined by means of an X-ray fluorescence micro-probe.

A form of alumina very effective as a support for nickel is γ-Al_2O_3, and transformation of alumina to α-Al_2O_3 is often a cause of loss of catalytic activity (Kaempfer 1975, Cusumano and others 1976, pp 32-33). Thus, methods of inhibiting α-Al_2O_3 formation are among those tried for stabilising Ni-Al_2O_3 catalysts. Stabilising by spinel-forming elements has been referred to (Section 2.1.4). It has been claimed that the presence of B_2O_3 in Al_2O_3 inhibits the formation of α-Al_2O_3 (McArthur 1974a, b, 1977a). Aluminium borate supports were prepared by calcining shaped composites of Al_2O_3 and B_2O_3 at 650°-1400°C for some hours, and these were impregnated with the desired metal by conventional techniques.

The effect of some supports with platinum and palladium as well as with nickel in methanation catalysts is to influence a shift as against the unsupported metal in selectivity towards formation of higher molecular weight hydrocarbons than methane (Vannice 1976b, 1977).

In a study of the relative reactivities of complexes represented by $(NH_4)_aMCl_6$ where M indicates Pd, Rh, Ru, Pt and Ir) towards γ Al_2O_3, it was found that the relative reactivities were $Pd > Rh > Ru >> Pt \simeq Ir$ (Summers and Ausen 1978).

The slightly increased resistance to sulphur poisoning conferred on nickel by a ZrO_2 support has already been referred to (Section 2.1.2).

From a study of the reduction of nickel oxide supported on Al_2O_3, SiO_2, SiO_2-Al_2O_3 and MgO it was concluded that there is probably reaction between NiO and the supports (Khasanov and others 1978, Nozawa and Shirasaki 1978). It also emerged that NiO impregnated into supports was more easily reduced than when produced in co-precipitation with the supports or in gel-mixing.

A US patent specification describes preparations purported to yield supported catalyst of controlled pore-size distribution (Mitchell and Whitehurst 1977). In an example methyl trichlorosilane is hydrolysed and the product processed successively with caustic soda and nickel chloride and aluminium chloride to produce material which after calcining is a nickel-aluminium silicon solid suitable, *inter alia,* as a methanation catalyst.

Novel carriers described are molten metal salts, melting below 1000°C and stable at 500°–800°C, in which an active metal catalyst is suspended in finely divided form (Kiovsky and Wald 1977a, b). Suitable salts include $ZnBr_2$, $ZnCl_2$, ZnI_2, mixtures of an iron halide with NaCl or KCl, and the ternary eutectic of Li_2CO_3, Na_2CO_3 and K_2CO_3. Effective active metals are zinc, manganese, molybdenum. Problems of carbon deposition and catalyst instability are stated to be minimal with the system, and because it is liquid heat removal from and temperature control of exothermic reactions are facilitated. Also, by absorbing water from the reactants the equilibrium state of the methanation reaction is shifted towards methane formation. A particular advantage lies in the possibility of regenerating the metal catalyst after poisoning by sulphur by separation and treatment.

2.9 Catalyst characterisation and testing

Proper understanding of catalytic phenomena requires satisfactory characterisation of catalytic materials and measurement of the physical and chemical properties that affect their catalytic activity, such as surface area, pore volume, pore size distribution, surface composition, surface morphology. Measurement of specific surface areas, i.e. areas occupied by individual components of a catalyst, is particularly important, as it is on this that the determination of specific activity or "turn over number" depends. The importance of relating reaction rate to surface area of the active component in a catalyst is shown by Vannice (1975a) in expressing some rate data in terms of unit surface area of active metal. On this basis iron, for example, which hitherto had been regarded as a poor methanation catalyst, was shown to be intrinsically more active than nickel.

Many of the papers in the proceedings of the 1975 symposium on catalyst preparation (Delmon and others 1976), already referred to, describe in some detail testing of the catalysts they describe, and catalyst characterisation, in particular measurements of gas adsorption and surface area, is dealt with fully by Vannice (1976a) and Cusumano, Dalla Betta and Levy (1976, pp 50-62). The latter discussed the use of X-ray diffraction, transmission electron microscopy and gas chemisorption techniques in determining specific surface area and discriminating between that of the active material and support.

Electron spectroscopy for chemical analysis (ESCA) has been used in the investigation of catalysts prepared by the coprecipitation of nickel and aluminium carbonates followed by calcination and reduction (Shalov and Reucroft 1977), and the magnetic properties of nickel catalysts have been studied, mainly with a view to characterisation (Everson and others 1976, Mulay and others 1976).

In view of the detailed treatment by the above authors the subjects of catalyst characterisation and testing are not considered further in this document except to mention that in the last few years papers have appeared dealing with differential scanning calorimetry (Beechcroft and others 1975), differential thermal analysis (DTA) (Beechcroft and other 1975, Zlobina and others 1973), differential contact potential (D'Yakonov and others 1970), magnetisation changes in studying catalysts (Rudajevova and Pour 1975), the differential photometric determination of nickel in catalysts (Lisenkova and others 1969), and the determination of the mechanical properties of catalysts (Le Page and Miquel 1976).

2.10 Mechanism

As stated in Section 1, although methanation is apparently a simple reaction, its mechanism over catalysts has not been established entirely unambiguously. Postulated mechanisms fall broadly into three categories (Mills and Steffgen 1973, Araki and Ponec 1976):

(i) Carbonyls are formed as intermediates.

(ii) Oxygen-containing intermediates are formed on the catalyst which are then hydrogenated to methane and water (Dalla Betta 1977, Farrauto 1976, Goddard and others 1977, Grigor'ev and others 1975, Lafer and others 1974, Martin and others 1977, Vannice 1975b and references in Table 10).

(iii) The reaction occurs through surface reactive carbidic carbon, produced by dissociative absorption of carbon monoxide on the catalyst surface (e.g. Araki and Ponec 1976, Ponec 1978, van Barneveld and Ponec 1978, Wentrick and others 1976a, b).

Theories under the first category are generally rejected because the carbonyls are unstable at the reaction temperatures usually employed.

Theories under category (ii) have been reviewed and discussed by Mills and Steffgen (1973), Vannice (1976a), and Cusumano and others (1976 pp 110-113); proposals for models incorporating oxygenated intermediates are summarised in Table 10 over page, taken from Vannice's paper. The models were proposed only for nickel, except model 5, although it was suggested that Model 1 might apply also to cobalt and iron.

Regarding model 1 it is suggested that with catalysts selective to the production of higher hydrocarbons rather than methane CH_2 polymerisation becomes predominant after the step $[S\text{-}HCOH]^+ + [S\text{-}H_2]^- \rightarrow S\text{–}CH_2 + H_2O + S$.

In model 5, y in the rate-determining step increases with increasing ability of the catalyst to produce higher molecular weight hydrocarbons (Cusumano and others 1976, pp 110-112), thus:

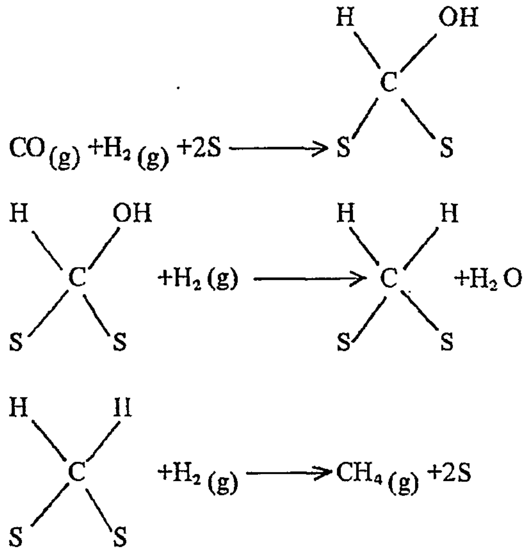
Metal	y
Pd	1
Ni	2
Co	3
Ru	4

It was also found that catalyst activity for methanation increased with strength of the H atom bond to the surface and decreased with strength of the CO bond. This is consistent with the model if it be assumed that the bond strength of the complex HCOH-metal surface is directly related to the strength of the CO bond to the metal: as the latter decreases the surface coverage of the complex would decrease and make more of the surface available to hydrogen; this would tend to equalise the surface coverages of HCOH complex and H_2, thereby increasing the rate of the rate-determining step.

From studies of the co-adsorption of hydrogen and carbon monoxide and the chemisorption and decomposition of formaldelyde and methanol on nickel and ruthernium it was postulated that oxygenated hydrocarbon complexes may play an important role in methanation on ruthenium but not on nickel (Yates and others 1977, Goodman and others 1978). However, later work has provided experimental evidence much more cogently favouring methanation models in which dissociative adsorption of CO on a catalyst produces active surface carbon as an intermediate (i.e. category (iii) above). The evidence is presented in papers cited after the statement of category (iii) at the beginning of this Section, 2-10. (It is of interest that in his review Ponec (1978) indicated that his researches into catalytic CO/H_2 reactions had begun with the idea that oxygen-containing intermediates do exist but he no longer had confidence in that theory).

The adsorption of CO on a nickel surface as a first step in the methanation mechanism has

Table 10. Kinetic models for the methanation reaction *(Vannice 1976a)*

	Proposed methanation model	Refs.
1.	$S + e^- + H_2 \longrightarrow [S\text{-}H_2]^-$ $S + CO \longrightarrow [S\text{-}CO]^+ + e^-$ $[S\text{-}CO]^+ + [S\text{-}H_2]^- \longrightarrow [S\text{-}HCOH]^+ + e^- + S\text{(RDS)}$ $[S\text{-}HCOH]^+ + [S\text{-}H_2]^- \longrightarrow S\text{-}CH_2 + H_2O + S$ $S\text{-}CH_2 + [S\text{-}H_2]^- \longrightarrow CH_4 + e^- + 2S$	Vlasenko and Yuzefovich 1969, Kozub and others 1965a, b
2.		Bousquet and others 1972
3.	$[H_2CO]_{(ad)} + H_{2(ad)} \longrightarrow CH_{2(ad)} + H_2O_{(ad)}$ (RDS) $H_2S \longrightarrow 2H'_{(ad)}$ or (RDS) $H_2 + 2S \longrightarrow 2H''_{(ad)}$	Schoubye 1969, Van Herwijnen and others 1973
4.	$CO + S \longleftrightarrow S\text{-}CO$ $H_2 + 2S \longleftrightarrow 2S\text{-}H$ $S\text{-}H + S\text{-}CO \longleftrightarrow S\text{-}HCO + S$ $S\text{-}H + S\text{-}HCO \longleftrightarrow S\text{-}H_2CO + S$ $S\text{-}H + S\text{-}H_2CO \longleftrightarrow S\text{-}H_3CO + S$ $S\text{-}H_3CO \longrightarrow$ products	Fontaine 1973
5.	$H_{2(g)} + CO_{(g)} \longrightarrow H\,COH_{(ad)}$ $H\,COH_{(ad)} + y/2H_{2(ad)} \longrightarrow CHy(ad) + H_2O_g$ (RDS) $CH_{y(ad)} + H_{2(ad)} \longrightarrow CH_{4(g)}$	Vannice 1975b

Note: S = empty metal surface site

RDS = rate determining step

been studied by a number of workers (e.g. Araki and Ponec 1976, Harberts and others 1977, Ponec 1978, Rabo and others 1978, van Dijk and others 1976, Wentrick and others 1976,b.)

It was concluded that dissociative chemisorption of CO on nickel is possible for the formation of a surface carbon intermediate in catalytic methanation. Distinction was made between highly reactive surface carbon, unreactive carbon and bulk Ni_3C. Wentrick and others (1976a, b) showed that the active surface carbon was bonded to the nickel as a carbidic-type surface species which converted to graphitic carbon of very low reactivity to hydrogenation at temperatures above 675K.

Rabo and others (1978) found that at atmospheric temperature CO adsorption on nickel was non-dissociative and the adsorbed CO was inert to hydrogenation. At 200° or 300°C, however, adsorption was mainly dissociative, resulting in a Ni-C species which reacted with hydrogen even at atmospheric temperature forming methane and higher homologues. At 300°C the surface carbon on nickel co-existed with chemisorbed CO, and, although the surface carbon was much more reactive to hydrogen than the undissociated CO, a small but significant proportion of the methane produced on hydrogenation was apparently derived from the latter.

Cobalt and ruthenium behaved similarly to nickel.

It has also been postulated that non-dissociatively adsorbed CO may be adsorbed on oxidised patches on a catalyst or in "on-top" positions where it competes with hydrogen adsorption (Biloen and others 1979).

Araki and Ponec (1976) used isotopically labelled carbon to demonstrate that surface carbon on a catalyst was an intermediate in methanation. Carbon isotope, ^{13}C, was deposited on a clean nickel film by disproportionation of ^{13}CO at 300°C. A mixture of hydrogen and ^{12}CO was then admitted under low pressure to the nickel at 250°C and the reaction followed. $^{13}CH_4$ was first produced by an initial fast reaction, $^{12}CH_4$ appearing after an induction period. It was argued that if an oxygenated complex (e.g. HCOH) was responsible for the fast methanation reaction $^{12}CH_4$ would have appeared first; $^{13}CH_4$ appearing first showed that the methanation reaction proceeded by dissociation of CO with active surface carbon an intermediate.

Experiments to compare Ni-Cu alloys with Ni as methanation catalysts have led to the conclusion that dissociative adsorption of CO requires sites in the form of ensembles of several Ni atoms where C atoms can be bound to several Ni atoms simultaneously (Araki and Ponec 1976, Ponec 1978, van Dijk and others 1976).

It has also been proposed that dissociation of CO is fast, i.e. kinetically not rate determining, in the presence of chemisorbed hydrogen, although slower in the absence of hydrogen (e.g. Biloen and others 1979).

Kinetic evidence is also available that over nickel dissociative adsorption of CO is the fastest or even the only methanation route (Rabo and others 1978, Wentrick and others 1976a,b).

It emerges that methanation over a nickel catalyst probably occurs through a surface carbon intermediate by a mechanism represented broadly by:

$$\left[\begin{array}{lll} & \text{(i)} & 2M + CO \rightarrow M{-}C + M{-}O \\ & \text{(iia)} & M{-}O + H_2 \rightarrow M + H_2O \\ (& \text{(iib)} & M{-}O + CO \rightarrow M + CO_2\,) \\ & \text{(iii)} & M{-}C + 2H_2 \rightarrow M + CH_4 \end{array}\right]$$

where M represents the catalyst surface.

This mechanism is very similar to that put forward by Fischer for the Fischer-Tropsch process.

Although the mechanism outlined above very probably represents the major methanation route it may not be the only one; as Rabo and others (1978) have shown a small proportion of the methane may be produced through chemisorbed, undissociated CO.

Sachtler, Kool and Ponec (1979) investigated whether cobalt and ruthenium as methanation catalysts behave with regard to surface carbon similarly to nickel. Using labelled ^{13}C in a technique similar to that of Araki and Ponec (1976), they found that carbon deposited on Co and Ru surfaces can be incorporated into CH_4 when a reaction mixture is admitted to the carburized surface; but they did not show unequivocally that this is the main route to CH_4 formation on those metals.

3. Methanation for hydrogen purification

The catalysts in the literature cited in this section were studied specifically as methanation catalysts for the removal of small concentrations of carbon oxides from hydrogen for its purification. However, there seems no reason for supposing that they would not be effective also in the methanation of a higher proportion of carbon monoxide for the production of rich fuel gas as described in the previous section.

3.1 Nickel

As already stated, nickel is the commonest hydrogenation catalyst, and most of the publications on the purification of hydrogen by catalytic methanation of carbon oxides in it are concerned with this metal.

Bridger and Woodward (1976) described the preparation of methanation catalysts for the purification of ammonia synthesis gas. The catalysts consisted essentially of nickel metal dispersed on a support of alumina mixed with other oxides. The presence of 2 to 3% of MgO was beneficial in limiting the growth of NiO during calcination in catalyst preparation. The life of a good catalyst was 3 to 5 years.

Randhava and others (1969b) studied the methanation of carbon monoxide in concentrations below 9500 ppm in hydrogen over a commercial precipitated catalyst consisting of 58% nickel on kieselguhr in pellet form, 3.175 x 3.175 mm. The rate of reaction could be expressed as

$$-r_{CO} = k(T)\, C_{CO}^{0.7}$$

where

k is the reaction rate constant
r_{CO} is the reaction rate
C_{CO} is the concentration for carbon monoxide

At low temperature k followed the Arrhenius temperature dependence; at higher temperature there was evidence of diffusion control of the reaction rate.

Another simple catalyst comprising 35% NiO on alumina was prepared by co-precipitation and mixing of basic nickel carbonate with Al_2O_3 in water or ammonia solution and then calcining at 400°C. The catalyst was stable at 550°C and its mechanical strength was reported as 39000 kN/m^2. At 130°C and at a space velocity of 4000 h^{-1} it reduced the carbon monoxide content of hydrogen to below 20 ppm (Kreindel and others 1972a).

Treatment of hydrogen containing carbon dioxide with a nickel catalyst on kieselguhr at 200–300°C, atmospheric pressure and space velocities of 500–4000h^{-1} reduced the carbon dioxide content from 2–10% to 25ppm (Masagutov and others 1976).

A Raney-type nickel catalyst containing 30–35% Ni, 5–18% Al and the balance $Al_2O_3 . 3H_2O$ was reported effective at 175°–250°C and at space velocities 9000–36000 h^{-1}, for the selective methanation of carbon monoxide in concentration up to 1% in hydrogen-carbon dioxide mixture (Randhava 1972). A method of manufacturing the catalyst is described which entails coating an inert support, such as Berl saddles, with an aqueous slurry of pulverised Al-Ni alloy and $Al(OH)_3$; drying the coating and heating the coated forms to at least 50°C; immersing the coated forms in water at 25-100°C; leaching the coated forms with alkali hydroxide to remove part of the aluminium and produce an active skeletal and nickel catalyst. The corresponding unsupported catalyst can be produced by leaching aluminium from an aluminium-nickel alloy with alkali hydroxide.

Studies (Berezina 1972b) were made of the efficacy of the following catalysts, after reduction with hydrogen at 230°–350°C, in removing oxides of carbon from hydrogen by methanation: a commercial Ni-Cr catalyst containing (a) 57% Ni; (b) a similar catalyst containing 46% Ni; (c) a Ni-Al-Cr catalyst containing 35% Ni; (d) a Ni-Cu-Zn-Al catalyst containing 37% Ni. The activities of the catalysts decreased in the order (c) > (b) > (a) > (d).

Three publications (Vahala 1971b, Banks 1973, Campbell and others 1972) illustrate the similarity in procedures that have been described for the preparation of nickel catalysts:

1. Banks described the preparation of catalysts containing nickel, silicon dioxide, alumina and silicon dioxide, magnesium oxide, chromium oxide and uranium oxide and alumina or containing cobalt and silicon dioxide. As an example, potassium carbonate solution was added to nickel nitrate solution and sodium water glass at 60–70°C. The precipitate, after drying at 120°C, was calcined at 450°C for 4 hours, pulverized to about 0.7 mm and pelletized with 2% graphite to give a nickel–silica catalyst. Gas of composition H_2 27.5, CO 0.9, CO_2 3.1, CH_4 55.4, C_2H_6 13.1% by treatment with the catalyst at 180°C and 1572 kPa with a space velocity of 5100 h^{-1} was converted to gas of composition H_2 13.2, CO_2 0.1, CH_4 70.9, C_2H_6 15.8%.

2. In a technique due to Campbell and others (1972), precipitated basic nickel carbonate was calcined at 350°C for 6 hours to produced nickel oxide, which was milled, mixed with laminated alumina, an aluminium-containing cement of low silica content, magnesium and powdered graphite. After pelletizing, the mixture was calcined at 400°C, steeped in water for 24 hours and dried. The mixture produced had the composition approximately NiO 25, Al_2O_3 50, SiO_2 2, CaO 15, MgO 2, Fe_2O_3 6%. The catalyst was activated by reduction in crude ammonia synthesis gas.

3. Vahala (1971b) investigated the preparation of thermally stable methanation catalysts by saturation of catalyst supports like kieselguhr and alumina with active catalyst precursors, by precipitation of active materials on support surfaces, and by co-precipitation of nickel salts with compounds of silica and aluminium. He concluded that a catalyst made by co-precipitation from water glass and nickel nitrate solution was thermally stable and about as active as one made by precipitating nickel (23%) on kieselguhr, which was more active than the corresponding nickel-chromia catalyst. Catalysts made by saturating alumina with nickel nitrate had low activity and low thermal stability. Catalysts prepared by co-precipitation of nickel nitrate and sodium aluminate were thermally stable at 600°C.

   Berezina and others (1972a) investigated the effects of thermal treatment in air, helium, hydrogen and a mixture of hydrogen and nitrogen on the initial catalyst mass during the preparation of nickel-chromium and nickel-aluminium-chromium catalysts. Ni-Cr compounds containing Cr^{6+} decomposed at 460°–580°C in an inert atmosphere, at 490°–600°C in air and at 190°–330°C in hydrogen. In the case of Ni-Al-Cr catalysts, calcination in air and in an inert gas decomposes the Ni-Cr compounds with the formation of a solid solution at 400°–450°C. Heat treatment in hydrogen leads to the reduction of the Ni-Cr compounds to Ni without thermal decomposition. The Ni-Cr catalyst was thermally stable at temperatures up to 400°C and the Ni-Al-Cr catalyst up to 500°C.

3.2 Iron

There is interest in iron methanation catalysts because they offer the possibility of using similar catalysts for purifying the hydrogen for ammonia synthesis as for the synthesis.

In a Russian patent specification (Dmitrienko and others 1972) the patentees describe the promotion of a methanation and ammonia synthesis catalyst by metal oxides in order to increase its contact surface area, thermal stability and resistance to poisoning. The catalyst comprised FeO 28-56%, Al_2O_3 0.5–11%, K_2O 0.7–1.5%, CaO 1.5–3.5%, SiO_2 below 1%, MgO below 5%, V_2O_5 below 5%, and the balance Fe_2O_3.

A Czech patent (Vahala and Janeck 1974) describes the preparation of an Fe_2O_3-Cr_2O_3-Al_2O_3 catalyst for the removal of oxides of carbon from crude hydrogen. Ammonium carbonate solution was added to solutions of technical grade or waste $FeSO_4$, $Cr_2(SO_4)_3$ and $Al_2(SO_4)_3$ at 45°C. The precipitate after washing and drying was ground to below 2mm, reduced for 6 hours in hydrogen at 480°C, passivated in nitrogen containing 1% air for 5 hours and tabletted with 3% graphite.

3.3 Nickel-iron

In discussing the purification of mixtures of nitrogen and hydrogen for ammonia synthesis, Sokol and others (1970) stated that Ni-Cr is a very efficient catalyst for the purpose, but is expensive and sensitive to catalyst poisons, and its pores are readily sealed by traces of oils in the synthesis gas stream. They recommended the use of a combination of Fe and Ni-Cr catalysts, the Fe serving as a precatalyzer and primarily as an adsorption filter trapping sulphur compounds and trace oils.

Similar catalysts are described in patent specifications. A German patent (Krabets and others 1971) refers to Fe-Ni catalysts containing Cr and Al broadly of the composition NiO : Fe_2O_3 : Cr_2O_3 : Al_2O_3 in the ratio 5-40 : 92-5 : 3-15 : 0-40. As an example of the preparation of such a catalyst, $Fe(NO_3)_2.9H_2O$, $Cr(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ in the proportions 3690, 344, 506 were mixed with 20% boehmite and 2% graphite and pelletted to size 5x5 mm. When hydrogen containing 100 ppm carbon monoxide and 200 ppm carbon dioxide was treated with the catalyst at 1324 kPa and 300°C at a space velocity of 2000 h^{-1}. the content of carbon oxides was reduced to less than 0.1 ppm carbon monoxide and 2 ppm carbon dioxide.

A catalyst useful for the removal of carbon oxides from ammonia synthesis gas contains Ni as NiO (15–50%), iron hydroxide and/or iron oxide (>15%), and alkali or alkaline earth metal compounds. With the catalyst conversion of carbon oxides to methane occurs at 100°–400°C. Thus, hydrogen initially containing 700 ppm carbon dioxide after passage over the catalyst at 190°C contained less than 10ppm carbon dioxide (Badische Anilin and Soda Fabrik 1971).

3.4 Rhodium and ruthenium

Amirali and Randhava (1970) studied the selective methanation of carbon monoxide in a mixture of hydrogen and carbon dioxide, containing 3000 ppm carbon monoxide, at 125–300°C over several catalysts. The objective was to reduce the monoxide content to below 100 ppm without affecting the concentration of the other components. Ruthenium was the most effective catalyst, followed closely by catalysts of the Raney nickel type. Catalysts prepared by co-precipitating nickel on supports were unsatisfactory.

The use of rhodium and ruthenium in the removal of small quantities of carbon monoxide in hydrogen purification is described in a US patent specification (Baker and others 1971). Carbon monoxide in low concentration (~100 ppm) in hydrogen and in admixture with carbon dioxide was selectively methanated over a rhodium or ruthenium catalyst on an alumina support at 100°–220°C and at a space velocity of 500-3000 h^{-1}. The preferred catalyst consisted of ruthenium deposited in a conventional manner on 3.175 mm alumina pellets. Suitable proportions of ruthenium were in the range 0.01 to 5%, 0.5% being the best.

It was reported that palladium and platinum do not selectively catalyze the methanation of carbon monoxide.

Another US patent specification (Fleming and Randhava 1974) describes the removal of mixtures of carbon monoxide and dioxide in low concentration in hydrogen by methanation at 100° to 175°C in the presence of catalysts of rhodium or ruthenium or alloys of these, admixed in each case with tungsten oxide. Catalysts, for example, might comprise essentially ruthenium with 0 to 50% of the ruthenium substituted by platinum and 5 to 20% by reduced amorphous tungsten oxide. By varying the rate of gas flow and temperature carbon monoxide can be methanated preferentially as against carbon dioxide or both oxides can be methanated completely and sequentially.

The patentees give the following example of the preparation of a catalyst. A mixture of rhodium chloride and ammonium or alkali metal metatungstate is mixed in aqueous medium with sodium or potassium borohydride. The resulting co-precipitated mixture, consisting essentially of rhodium and amorphous tungsten oxide, is combined with (a) an aqueous dispersion of binder-water-proofing agent, such as PTFE, (b) mineral oil to form a catalyst paste.

Randhava and Rehmat (1970), investigating the hydrogenation of carbon dioxide in concentrations below 3600 ppm in hydrogen over a catalyst containing 0.5% ruthenium, found that the carbon dioxide reacted to form carbon monoxide which was then hydrogenated to methane. The empirical rate expression for the conversion was

$$r_{CO_2} = kC_{CO_2}^{1.5}$$

where k obeyed the Arrhenius temperature dependence. Increasing carbon dioxide concentration decreased the value of the reaction constant k while the activation energy remained unchanged.

In an earlier paper Randhava and others (1969a) reported a similar expression ($-r_{CO} = kC_{CO}$) for the methanation of CO in low concentration over a ruthenium catalyst. They used a commercial catalyst comprising 0.5% ruthenium impregnated on alumina pellets (3.175x3.175 mm cylinders), weighing on average 0.044 g each. The bed was activated by passing He through the bed for 6 hours at 400°C.

4. Conclusions

(i) Nickel, particularly as Raney nickel or when supported on alumina, is still the most useful methanation catalyst. It is very active and at proper reaction temperature is selective towards the formation of methane in preference to higher hydrocarbons. Its main disadvantage is its susceptibility to poisoning by sulphur compounds in synthesis gas. The mechanism is not completely understood, but there is strong evidence that methanation over a nickel catalyst proceeds by way of active surface carbon produced by disproportionation of carbon monoxide.

(ii) Iron can be used as a methanation catalyst, but its selectivity to methane formation is not high, and, although its intrinsic reactivity is high, iron-containing catalysts as usually encountered are much less active than nickel catalysts. In some circumstances it may be advantageous to use an iron catalyst in the purification of ammonia synthesis gas since the same catalyst could be used for synthesis as for purification.

(iii) "Noble" metals of Group VIII are effective methanation catalysts. Ruthenium in particular is intrinsically very reactive, but because of its cost is normally encountered at attenuation of only 0.5% of its support, at which it is not really superior to nickel.

(iv) The primary problems of methanation catalysts relate to sulphur poisoning and stability: The best catalysts are very susceptible to sulphur poisoning, and although their life is acceptable, improvement is desirable. Molybdenum and tungsten catalysts are sulphur resistant, but their activity is not high nor are they very selective to methane formation. Solution of the sulphur problem, of course, would be furthered by a better understanding of the basic mechanism of catalytic methanation, particularly of the surface properties important to catalysis. At present there is not a clear understanding of the nature of sulphur poisoning of catalytic materials, and research is needed to clarify the mechanism of the interaction between sulphur and catalyst and the effect on surface reactions.

Investigations are also needed into the part catalyst supports can play in enhancing sulphur resistance.

Homogeneous methanation catalysts, if further developed may go some way to surmounting the difficulty of sulphur poisoning, and satisfactory methods of regenerating sulphur-poisoned catalysts may be discovered and developed.

Regarding thermal stability, the nature of catalyst sintering, interaction of active catalyst material with support, interactions within the catalyst support and between the main support and additives, and the effect of particle size are among factors that would repay investigation. Important aspects are inhibition of nickel sintering in catalysts and the interaction of Ni/NiO with the support.

(v) The technique of preparing a catalyst can affect its properties. At present this seems to be carried out on an empirical, as distinct to a strictly scientific, basis. Perhaps more work devoted simply to studies of technique variables might be profitable along, for example, the lines of Cervello and others (1976) referred to in Section 2.8.

(vi) Within limits the higher the temperature at which the heat of methanation is released the more effectively can it contribute to the overall efficiency of a conversion process (e.g. coal to SNG). At present the upper temperature limit for normal commercial operation is 450°C, so there is need for the development of a methanation catalyst capable of operation for long periods at temperatures considerably higher than this. At such temperatures the attainment of optimum equilibrium conditions might require elevated pressures, but with suitable catalysts operation at higher temperatures and moderately raised pressure might prove economically advantageous.

At high temperature there would be increased tendency for the deposition of unreactive carbon on the catalyst, but measures could no doubt be taken to counter this (e.g. by the controlled addition of H_2O).

The development of means of regenerating catalysts operating at high temperature might be advantageous or even necessary, although at high temperature the sulphur problem might be diminished.

5. References

ABIDOV, M.; MUNAVAROV, K (1977)
Aluminium · nickel catalyst for carbon dioxide conversion of natural gas.
USSR Patent 582,828; (5 Dec 1977)

ALCORN, W.R.; CULLO, L.A. (1976)
Nickel-copper-molybdenum methanation catalyst
U.S. Patent 3,962,140; 8pp (8 Jun 1976)

ALPERT, S.B.; SHERWIN, M.B.; COCHRAN, N.P. (1976)
Slurry phase methanation process
US Patent 3, 989, 734; 4 pp (2 Nov 1976)

AMIRALI, A.; RANDHAVA, S.S. (1970)
Selective methanation of carbon monoxide.
Industrial and Engineering Chemistry, Product Research and Development; 9 (4); 512-515 (Dec 1970)

ANDERSON, K.J.; CANDIA, H.R.; ROSTRUP-NIELSON, J. (1976)
Catalyst for preparing methane-rich gases
German Patent 2, 529, 316; 18 pp (22 Jan 1976)

ARAKI, M.; PONEC, V. (1976)
Methanation of carbon monoxide on nickel and nickel-copper alloys
Journal of Catalysis; 44 (3); 439-448 (1976)

ATKINSON, G.B.; NICKS, L.J. (1976)
Preparation and use of high surface area transition metal catalysts.
U.S. Patent Application 738,201; 17pp (3 Nov 1976)

ATKINSON, G.B.; NICKS, L.J. (1977)
Mischmetal-nickel alloys as methanation catalysts
Journal of Catalysis; 46 (3); 417-419 (1977)

BADISCHE ANILIN AND SODA FABRIK, AKT. (1971)
Catalytic methanisation of carbon monoxide and/or carbon dioxide in gases containing hydrogen.
British Patent 1,236,618; 4 pp (23 Jun 1971)

BAIRD, M.J.; STEFGEN, F.W. (1977)
Methanation studies on nickel-aluminium flame-sprayed catalysts
Industrial and Engineering Chemistry, Product Research and Development; 16 (2); 142-147 (Jun 1977)

BAKER, B.S.; HUEBLER, J.; LINDEN, H.R.; MEEK, J. (1971)
Selective removal by methanation of carbon monoxide from a mixture of gases containing carbon dioxide
US Patent 3,615,164; 8pp (26 Oct 1971)

BANKS, R.G.S. (1973)
Substitute for natural gas
German Patent 2,257,239; 13 pp (30 May 1973)

BARCICKI, J.; GRZEGORCZYK, W.; BOROWIECKI, T.; NAZIMEK, D.; DENIS, A. (1977)
Activation of model nickel catalyst for hydrogenating carbon dioxide into methane
Chemische Tecknik (Leipzig); 29 (9); 497-500 (1977)

BARTHOLOMEW, C.H. (1975)
Alloy catalysts with monolith supports for methanation of coal-derived gases
Quarterly Technical Report; 22 Apr–22 Jul 1975; FE-1790-1, Provo, Utah, Brigham Young University, 74 pp (6 Aug 1975)

BARTOLOMEW, C.H.; BARTON, W.B. (1976)
Mathanation activity of supported nickel alloys
American Chemical Society, Division of Fuel Chemistry; 24 (4); 30-42 (1976)

BEECHCROFT, T.; MILLER, A.W.; ROSS, J.R.H. (1975)
Use of differential scanning calorimetry in catalyst studies. Methanation of carbon monoxide over nickel/alumina catalysts.
Journal of Catalysts; 40 (2); 281-285 (1975)

BEREZINA, Yu. I.; CHESNOKOVA, R.V.; BONDAREVA, A.A.; CHISTYAKOVA, G.A.; LYUDKOVSKAYA, B.G. (1972 a)
Catalysts for the purification of gases by removal of oxygen and oxygen-containing impurities. (ii) Heat treatment of the catalyst.
Trudy Naucho-issledovatel 'nogo Proektnogo Instituta Azotnoi Promyshlennosti Produktivnykh Organov Sinteza; (17); 204-217 (1972)

BEREZINA, Yu. I.; NECHUEVA, L.G.; ZHIGAL'TSOV, K.P.; SCHUMILKINA, V.A. (1972b)
Catalyst for the fine purification of gases by removal of oxygen and oxygen-containing impurities.
(iv) Side reactions of carbon monoxide oxidation in the methanation of carbon monoxide.
Trudy Naucho-issledovatel'nogo Proektnogo Instituta Azotnoi Promyshlennosti Produktivnykh Organov Sinteza; (17); 223-234 (1972)

BERNARDO, C.A.; TRIMM, D.L. (1979)
The kinetics of gasification of carbon deposited on nickel catalysts
Carbon; 17(2); 115-120 (1979)

BIENSTOCK, D.; FIELD, J.H.; FORNEY, A.J.; DEMSKI, R.J. (1961)
Pilot plant development of the hot-gas-recycle process for the synthesis of high Btu gas
US Bureau of Mines, Report of Investigations, R15841, 27pp. (1961)

BILOEN, P.; HELLE, J.N.; SACHTLER, W.M.H. (1979)
Incorporation of surface carbon into hydrocarbons during Fischer-Tropsch synthesis: mechanistic implications
Journal of Catalysis; 58; 95-107 (1979)

BLAND, J.L. (1975)
Metallic catalyst
US Patent 3, 876,557; 5 pp (8 Apr 1975)

BLUM, D.B.; FRANK, M.E.; SHERWIN, M.B. (1974)
Liquid phase methanation PDU results
In: *Proceeding of the Sixth Synthetic Pipeline Gas Symposium:* Chicago, Ill., Oct 1974, 77-94 (1974)

BOUSQUET, J.L.; TEICHNER, S.J. (1972)
Carbon monoxide methanation in the presence of catalysts prepared from nickel hydroaluminate.
I Reaction kinetics
Bulletin Société Chimique de France; (10); 3689-3692 (1972)

BOUSQUET, J.L.; GRAVELLE, P.Ch.; TEICHNER, S.J. (1972)
Methanation of carbon monoxide by hydrogen in contact with catalysts from nickel hydroaluminate.
III Reaction mechanism
Bulletin Société Chimique de France; (10); 3693-3700 (1972)

BRIDGER, G.W.; WOODWARD, C. (1976)
Production of methanation catalysts In: DELMON, B.; JACOBS, P.A.; PONCELET, G. (eds)
Preparation of catalysts
Amsterdam, Oxford, New York, Elsevier Scientific Publishing Company (1976)

BROECKER, F.J.; KAEMPFER, K.; SCHWARZMANN, M.; MAROSI, L. (1974a)
Catalyst for the production of methane from carbon monoxide - and hydrogen-containing gases
German Patent 2,231,316; 21 pp (10 Jan 1974)

BROECKER, F.J.; KAEMPFER, K.; SCHWARZMANN, M.; MAROSI, L. (1974b)
Catalyst and its use in methane production
German Patent 2,231,317; 22 pp (10 Jan 1974)

BROECKER, F.; DETHLEFSEN, W.; KAEMPFER, K.; MARUSI, L.; SCHWARZMANN, M.; TRIEBSKORN, B.; GUENTER, Z. (1974c)
Catalyst and its use in preparing methane from carbon monoxide- and hydrogen-containing gases
German Patent 2, 255, 877; 26pp (16 May 1974)

BROECKER, F.J.; SCHWARZMANN, M.; KAEMPFER, K. (1976)
Hydraulic binder-containing catalyst and its use in the methanation of gases containing carbon oxides and hydrogen
German Patent 2,461,482; 18 pp (8 Jul 1976)

CAMPBELL, J.S.; DAVIES, P.; RICHMOND, J.R. (1972)
Methanation catalyst
German Patent 2,150,387; 15 pp (10 May 1972)

CATALYST AND CHEMICALS, INC. (1970)
Pellet catalysts for methane production
German Patent 1 938 079; 25 pp (19 Mar 1970)

CERVELLO, J.; HERMANA, E.; JIMENEZ, J.F.; MELO, F. (1976)
Effect of the impregnation conditions on the internal distribution of the active species of catalysts
In: DELMON, B.; JACOBS, P.A.; PONCELET, G. (eds)
Preparation of catalysts
Amsterdam, Oxford, New York, Elsevier Publishing Company (1976)

CHERNYSHEV, A.B.; GUDKOV, S.F. (1956)
The mechanism of methane synthesis on a fluidized nickel catalyst
A.B. Chernyshev, Izbranne Trudy; 305-310 (1956)

COBZARU, A.; MIHAI, A.; MUSCA, G. (1971)
Catalyst for the conversion of carbon monoxide into methane
Romanian Patent 53,565; 2 pp (18 Nov 1971)

CRATTY, L.E.; RUSSELL, W.W. (1958)
Nickel, copper and some of their alloys as catalysts for the hydrogenation of carbon dioxide
Journal of the American Chemical Society; 80 (4); 767-773 (1958)

CUSUMANO, J.A.; DALLA BETTA, R.A.; LEVY, R.B. (1976)
Scientific resources relevant to the catalytic problem in the conversion of coal
ERDA Final Report FE-2017-1
Palo Alto, California, Catalytica Associates Inc.; 565pp (Oct 1976)

DALLA BETTA, R.A.; SHELEF, M. (1976)
Heterogeneous methanation: effects of carbon, sulphur and water on activity measurements at various temperatures
American Chemical Society, Division of Fuel Chemistry, Preprints; 21 (4); 43-57 (1976)

DELLA BETTA, R.A.; SHELEF, M. (1977)
Heterogeneous methanation: absence of hydrogen – deuterium kinetic isotope effect on nickel, ruthenium, and platinum
Journal of catalysis; 49 (3); 383-385 (1977)

DALLA BETTA, R.A.; PIKEN, A.G.; SHELEF, M. (1974)
Heterogeneous methanation. Initial rate of carbon monoxide hydrogenation on supported ruthenium and nickel
Journal of Catalysis; 35 (1); 54-60 (1974)

DALLA BETTA, R.A.; PIKEN, A.G.; SHELEF, M. (1975)
Heterogeneous methanation: Steady-state rate of carbon monoxide hydrogenation on supported ruthenium, nickel and rhenium
Journal of Catalysis; 40 (2); 173-183 (1975)

DALLA BETTA, R.A.; PIKEN, A.G.; SHELEF, M. (1976)
Methanation catalyst
German Patent 2, 619, 325; 10 pp (11 Nov 1976)

DELMON, B.; JACOBS, P.A.; PONCELET, G. (eds) (1976)
Preparation of catalysts
Amsterdam, Oxford, New York, Elservier Scientific Publishing Company, xvi + 706pp (1976)

DERGACHEV, A.A.; SILAKOVA, A.A.; VASSERBERG, V.E. (1972)
Nickel-alumina catalysts obtained by controlled adsorption from the gas phase
Khimicheskaya Promyshlennost (Moscow); 48 (10); 756-758 (1972)

DERGACHEV, A.A.; SILAKOVA, A.A.; VASSERBERG, V.E. (1973)
Differential use of an aluminium oxide surface during the preparation of complex and mixed catalysts.
4. Ni-alumina catalysts, preparation methods and activity in the hydrogenation of carbon dioxide to methane
Izuestiya Akademiinauk SSSR: Slriya Khimichlskaya; 4;755-761 (1973)

DEW, J.N.; WHITE, R.R; SLIEPCEVICH, C.M. (1955)
Hydrogenation of carbon dioxide on a nickel-kieselguhr catalyst
Industrial and Engineering Chemistry; 47 (1); 140-146 (1955)

DICK, A.L. (1973)
Ruthenium – zinc oxide catalysts for methanation of liquid hydrocarbons
German Patent 2,303,904; 36 pp (2 Aug 1973)

DIEHL, E.K.; STEWART, D.L.; STREETER, R.C. (1974)
Progress in fluidized-bed methanation
Proceedings of the Sixth Synthetic Pipeline Gas Symposium, Chicago, Ill., Oct 1974, 95-112 (1974)

DIRKSEN, H.A.; LINDEN, H.R. (1963)
Pipeline gas from coal by methanation of synthesis gas
Institute of Gas Technology, Research Bulletin; (31); 137 pp (1963)

DMITRIENKO, L.M.; RABINE, P.D.; KUZNETSOV, L.D., MISHCHENKO, Sh. Sh.; LOPUKHOV, G.A.; IVANNIKOV, V.V.; LYASHCHENKO, A.I.; KHODAK, P.A.; KRIVENKO, I.P. (1972)
Iron catalyst for synthesis of ammonia and for methanation
USSR Patent 270,702; 2 pp (21 Apr 1972)

DOESBURG, E.B.M.; ORR, S.; ROSS, J.R.H.; VAN REIJEN, L.L. (1977)
Effect of temperature of reduction on the activity and selectivity of a coprecipitated nickel-aluminium catalyst for the Fischer-Tropsch and methanation reactions
Journal of the Chemical Society, Chemical Communications; (20); 734-735 (1977)

D'YAKONOV, Ya. I.; EGEUBAER, S.Kh.; MAKSIMOVA, N.P.; RUDNITSKII, L.A.; ALEKSEEV, A.M. (1970)
Study of nickel-magnesium catalysts by a contact potential difference method
Trudy Naucho-issledovatel'nogo Proektnogo Instituta Azotnoi Promyshlennosti Produktivnykh Organov Sinteza; (3); 89-91 (1970)

D'YAKONOV, YA. I.; EGEUBAEV, S. Kh.; SHISHKOVA, V.N.; MIRNOVA, G.M. (1971)
Nickel-magnesium catalysts
Trudy Naucho-issledovatel'nogo Proektnogo Instituta Azotnoi Promyshlennosti Produktivnykh Organov Sinteza; (11); 111-118 (1971)

ELATTAR, A.; TAKESHITA, T.; WALLACE, W.E.; CRAIG, R.S. (1977)
Intermetallic compounds of the type metal - nickel (MNi_5) as
Science; 196 (4294); 1093-1094(1977)

EVERSON, R.C.; MULAY, L.N.; MAHAJAN, O.P.; WALKER, P.L. (1976)
Magnetic and catalytic properties of sintered nickel catalysts for the methanation reaction
Second National Meeting, South African Institution of Chemical Engineers; Paper 3b, 14 pp (1976)

FARRAUTO, R.J. (1976)
Adsorption studies on a nickel-alumina methanation catalyst
Journal of Catalysis; 41 (3); 482-485 (1976)

FIELD, J.H.; DEMETER, J.J.; FORNEY, A.J.; BIENSTOCK, D. (1964)
Development of catalysts and reactor systems for methanation
Industrial and Engineering Chemistry, Product Research and Development; 3; 150-153 (1964)

FINCH, J.N.; RIPLEY, D.L. (1976)
Methanation of hydrogen and carbon monoxide
US Patent 3,988,334; 5pp (26 Oct 1976)

FLEMING, D.K.; RANDHAVA S.S. (1974)
Methanation of carbon monoxide and carbon dioxide
US Patent 3.787,468; 5pp (22 Jan 1974)

FLEMING, D.K.; RANDHAVA, S.S.; CAMARA, E.H. (1975)
Ruthenium – reduced amorphous tungsten oxide catalyst
US Patent 3,884,838; 11pp (20 May 1975)

FONTAINE, R. (1973)
Kinetics of the methanation of carbon monoxide over nickel catalysts
Ph.D Dissertation, Cornell University, 1973

FRANZ, W.F.; HESS, H.V. (1973)
Catalytic production of methane-rich fuel gas
US Patent 3, 759, 679; 4pp. (18 Sep 1973)

FREMERY, M.; REINER, R.; FOERSTER, F. (1976)
Reacting carbon monoxide and hydrogen to produce methane-containing gas
German Patent 2, 510, 164; 7 pp (16 Sep 1976)

FREMERY, M.; FOERSTER, F.; GUENTHER, P.; KANZLER, K.H. (1978)
Methanization of carbon monoxide by reaction with hydrogen
German Patent. 2, 705, 752; 9 pp (17 Aug 1978)

FUJIMOTO, K.; HASHIMOTO, H.; KUNUGI, T. (1978)
Hydrogenation of carbon monoxide over supported palladium catalysts
Sekiyu Gakki Shi; 21 (2); 135-8 (1978).

FUKUI, Y.; HIRAGA, R.; HATAYA, F.; SASAKI, R.; NAKAJIMA, F.; MATSUDA, S.; TONAMI, M. (1976)
Methanation reactor having multiple tubes internally coated with a catalyst
Japanese Patent 76 55, 780; 7 pp (17 May 1976)

FUKUI, Y.; ISHIZUKA, H.; HATAYA, F.; SASAKI, R.; NAKAJIMA, F.; KAWAGOE, H. (1977)
High strength ductile composites with catalyst layer
Japanese Patent 77 35, 784; 7 pp (18 Mar 1977)

GALSTAUN, L.S. (1977)
Methanation of gases containing high concentrations of carbon monoxide
Canadian Patent 1, 003,216; 22 pp (11 Jan 1977)

GENT, C.W.; ADSETTS, J.R.; FARMERY, K.; WOODWARD, C. (1975)
Methane-containing gas
German Patent 2,524,636; 33 pp (11 Dec. 1975)

GODDARD, W.A.; WALCH, S.P.; RAPPE, A.K.; UPTON, T.H.; MELIUS, C.F. (1977)
Methanation of carbon monoxide over a nickel catalyst; a theoretical study
Journal of Vacuum Science and Technology; 14(1); 416-418 (1977)

GOLEBIOWSKI, A.; PALUCH, S.; JANECKI, Z.; POLANSKI, A.; HENNEL, W.; ZIELINSKI, J.; WARZEC, C.; LISOWSKI, W. (1977a)
Catalytic tubes with well-supported catalyst, particularly for steam reforming of hydrocarbons and methanation
US Patent 4,019,969; 4pp (26 Apr 1977)

GOLEBIOWSKI, A.; PALUCH, S.; JANECKI, Z.; POLANSKI, A.; HENNEL, W.; ZIELINSKI, J.; WARZEC, C.; LISOWSKI, W. (1977b)
Catalytic tubes with solid bound catalyst, especially for reforming hydrocarbons and recovering methane
German Patent 2, 552, 646; 15 pp (26 May 1977)

GOLEBIOWSKI, A.; ROMOTOWSKI, T.; HENNEL, W.; WROBLEWSKA, T.; POLANSKI, A.; JANECKI, Z.; PALAUCH, S. (1977c)
Catalysts for vapour reforming of hydrocarbons and recovering methane
German Patent 2 552, 645; 13 pp (26 May 1977)

GOLEBIOWSKI, A; ROMOTOWSKI, T.; HENNEL, W.; WROBLEWSKA, T.; POLANSKI, A.; JANECKI,Z.: PALUCH, S. (1977d)
Catalyst for steam reforming of hydrocarbons and methanation
Polish Patent 94,829; 3 pp (30th Dec. 1977)

GOODMAN, D.W.; YATES, J.T.; MADEY, T.E. (1978)
Interaction of methanol with ruthenium
Chemical Physics Letters; 53 (3); 479-482 (1978)

GRACE, W.R. and Co (1976)
Methanation catalyst and its use
Japanese Patent 76, 116, 191; 9 pp (13 Oct 1976)

GRIGOR'EV, V.V.; ALEKSEEV, A.M.; GOLOSMAN, E.Z.; SOBOLEVSKII, V.S.; YAKERSON, V.I. (1975)
Adsorption of hydrogen and carbon oxides and mechanism of methanation over nickel catalysts
Kinetika i Kataliz; 16 (4); 975-978 (1975)

GUDKOV, S.F.; CHERNYSHEV, A.B. (1955)
A study of methane synthesis with a fluidized catalyst
Izvestiya Akademii Nauk SSSR : Otdelenie Tekhnicheskikh Nauk; (5); 154-156 (1955)

HAMMER, H.; IBRAHIM, I. (1976)
Methanation catalysts
German Patent 2,519,580; 10 pp (18 Nov 1976)

HAMMER, H.; HAKIM, I. (1978)
Boron-containing nickel catalysts for methanation of carbon monoxide
Chemie-Ingenieur-Technik; 50 (8); 622-623 (1978)

HANSBERGER, A.L.; HAMMONS, G.A. (1977)
Methanation process for the production of an alternate fuel for natural gas
US Patent 4, 005, 996; 12 pp (1 Feb 1977)

HANSFORD, R.C. (1976)
Thermally stable coprecipitated catalysts useful for methanation and other reactions.
US Patent 3,988,263; 7pp (26 Oct 1976)

HARBERTS, J.M.C.; BOURGONJE, A.F.; STEPHAN, J.J.; PONEC, V. (1977)
Adsorption and desorption of carbon monoxide from nickel and nickel/copper alloys
Journal of Catalysis; 47(1); 92-99 (Apr 1977)

HARRIS, N.; FOWLER, R. (1975)
Methane by fuel gas methanation
German Patent 2, 432, 885; 13 pp (6 Feb 1975)

HAYNES, W.P.; ELLIOTT, J.J.; FORNEY, A.J. (1972)
Experience with methanation catalysts
American Chemical Society, Division of Fuel Chemistry, Preprints; 16(2); 47-63 (1972)

HAYNES, W.P.; FORNEY, A.J.; ELLIOTT, J.J.; PENNLINE, H.W. (1974)
Synthesis of methane in hot gas recycle reactor: pilot plant tests
American Chemical Society Division of Fuel Chemistry, Preprints; 19 (3) 10-19 (Sep 1974)

HUFFMAN, J.C.; STONE, J.G.; KRUSELL, W.C.; CAULTON, K.G. (1977)
Homogeneous hydrogenation of carbon monoxide
Journal of the American Chemical Society; 99 (17); 5829-5831 (1977)

IMPERIAL CHEMICAL INDUSTRIES LTD (1970)
Catalyst handbook wtih special reference to unit precesses in ammonia and hydrogen manufacture
London, Wolfe, 119 (1970)

IMPERIAL CHEMICAL INDUSTRIES LTD. (1976)
Natural gas substitute from methanol
Japanese Patent 76 08, 303; 7 pp (23 Jan 1976)

INSTYTUT NAWOZOW SZTUCZNYCH (1977)
Nickel catalyst for gas-phase reforming of hydrocarbons and methanation
Japanese Patent 77 63,888; 5 pp (26 May 1977)

INUI, T.; FUNABIKI, M. (1978)
Hydrogenation on a supported polygenous composite catalyst.. I. Methanation of carbon dioxide and carbon monoxide on a supported nickel-lanthanum oxide - ruthenium catalyst
Chemistry Letters; (3); 251-252 (1978)

INUI, T.; FUNABIKI, M.: SUEHIRO, M.; SEZUME, T.; IWANA, T. (1978)
Hydrogenation on supported polygenous composite catalyst. II. Methanation of carbon dioxide and carbon monoxide over supported nickel-lanthanum oxide - ruthenium catalysts
Nippon Kagaku Kaishi; (4); 517-524 (1978)

JELINK, J.; KADLEC, J.; VEPREK, J. (1969)
Catalyst for selective hydrogenation of aldehydes and methanation of carbon monoxide and carbondioxide
Czechoslovakian Patent 132,071; 3 pp (15 Apr 1969)

JOHNSON, M.M.; TABLER, D.C.; NOWACK, G.P. (1977)
Substitute natural gas from gasification of coal char
US Patent 4,011,058; 7 pp (8 Mar 1977)

KAEMPFER, K. (1975)
Development of new catalysts for the manufacture of S.N.G.
Compendium Deutsche Gesellschaft fuer Mineraloelwissenschaft und Kohlenchemie; 24th 1974; 1; 367-378 (1975). *(Chemical Abstracts;* 83, No. 166558b)

KANG, C.C.C. (1976)
Catalyst for the production of hydrogen and/or methane
US Patent 3, 945, 944; 8 pp (23 Mar 1976)

KATO, A.; KAWAGOSHI, H.; MATSUDA, S.; NAKAJIMA, F. (1976)
Methane formation from hydrogen and carbon monoxide
Japanese Patent 76 75003; 5 pp (29 Jun 1976)

KESTER, F.L. (1974)
Hydrogenation of carbon dioxide over a supported ruthenium catalyst
American Chemical Society: Division of Fuel Chemistry, Preprints; 19 (1); 146-156 (1974).

KHASANOV, F.N.; VOROB'EV, V.N.; SVENTSITSKII, E.S.; TALIPOV, G.Sh. (1978)
Effect of preparation processes on the state of nickel ions in aluminium oxide – nickel oxide catalysts based on electron spectroscopic data
Zhurnal Prikladnoi Khimii (Leningrad); 51 (4); 784-789 (1978)

KHERA, S.S. (1976)
Process and catalyst for synthesizing a gaseous hydrocarbon mixture having a high methane content from carbon monoxide and hydrogen
US Patent 3,997,582; 8pp (14 Dec 1976)

KIOVSKY, T.E.; WALD, M.M. (1977a)
Methanation catalyst recovery
US Patent 4,006,177; 7 pp (1 Feb 1977)

KIOVSKY, T.E.; WALD, M.M. (1977b)
High temperature methanation with molten salt-based catalyst systems
US Patent 4,045,461; 8 pp (30 Aug 1977)

KOBYLINSKI, T.P.; SWIFT, H.E. (1976)
Metal chrysotile methane synthesis catalyst
US Patent 3,947,483; 6 pp (30 Mar 1976)

KOBYLINSKI, T.P.; SWIFT, H.E. (1977)
Metal chrysotile methane synthesis catalyst
US Patent 4,022,810; 6 pp (10 May 1977)

KOZUB, G.M.; RUSOV, M.T.; VLASENKO, V.M. (1965a)
A study of the electronic state of catalysts during adsorption and catalysis. (ii) Mechanism of hydrogenation of carbon monoxide on nickel catalysts
Kinetika i Kataliz; 6 (2); 224-249 (1965)

KOZUB, G.M.; RUSOV, M.T.; VLASENKO, V.M. (1965b)
A study of the electronic state of catalysts during adsorption and catalysis. (iii) Mechanism of carbon dioxide hydrogenation over a nickel catalyst
Kinetika i Kataliz; 6 (3); 556-568 (1965)

KRABETS, R.; KROME, H.; OESTREICHER, E. (1971)
Catalysts for the removal of small amounts of carbon monoxide and carbon dioxide from hydrogen-containing gases
German Patent 2,008,937; 6pp (9 Sep 1971)

KREINDEL, A.I.; SOBOLEVSKII, V.S.; YAKERSON, V.I.; GOLOSMAN, E.Z.; BOEVSKAYA, E.A.; GOLOVKOVA, A.I. (1972a)
Development of catalyst production methods for methanation (removal of carbon monoxide and carbon dioxide for hydrogen-containing gases)
Gazovaya promyshlennost; 17(5); 49 (1972)

KREINDEL,A.I.; SOBOLEVSKII,V.S.; YAKERSON,V.I.; GOLOVKOVA,A.I.; VARLAMOVA,A.M.; GOLOSMAN,E.Z.; KOROVIN,N.I.; KRAVCHENKO,F.F. (1972b)
Activity of mixed nickel catalysts for methanation (removal of carbon monoxide and carbon dioxide from hydrogen-containing gases)
Gazovaya promyshlennost; 17(8); 42-43 (1972)

KREINDEL, A.I.; SOBOLEVSKII, V.S.; GOLOSMAN, E.Z.; YAKERSON, V.I. (1974)
Catalytic activity of nickel catalysts on different supports during the hydrogenation of carbon monoxide
Kinetika i Kataliz; 15 (2); 408-412 (1974)

KURITA, H.; TSUTSUMI, Y. (1961)
Hydrogenation of carbon monoxide in the presence of the borides of nickel, cobalt and iron
Nippon Kogaku Zasslii; 82, 1461-1463 (1961)

LAFER, L.I.; DYKH, Zh. L.; LEVINA, V.V.; GRIGOR'EV, V.V.; YAKERSON, V.I.; RUBINSHTEIN, A.M. (1974)
Study of the adsorption and reaction mechanism of carbon monoxide and molecular hydrogen on the surface of nickel catalysts
Tezizy Dokladov Vsesoynzogo Seminariva "Primen'itelnnya Opticheskaya Spektroskopiya Adsorbtsii Katalistov"; 3rd Thesis; 29-30 (1974)

LALANCETTE, J.M. (1974)
Methanation
U.S. Patent 3,847,963; 4 pp (12 Nov 1974)

LALANCETTE, J.M. (1975)
Methanation processes
Canadian Patent 979,911; 12 pp (16 Dec 1975)

LARSON, F.G; SNAPE, E. (1974)
Nickel catalyst
U.S. Patent 3, 846, 344; 4 pp (5 Nov 1974)

LE PAGE, J.F.; MIQUEL, J. (1976)
Determining mechanical properties of industrial catalysts: correlations with their morphological and physical-chemical properties
In: DELMON, B.; JACOBS, P.A.; PONCELET, G. (eds)
Preparation of catalysts
Amsterdam, Oxford, New York, Elsevier Scientific Publishing Company (1976)

LISENKOVA, V.P.; YAKOVLEVA, P.F.; LAPINA, Z.V.; TSUNEVA, A.G. (1969)
Differential photometric determination of nickel in methane – production catalysts
Informatsionniye Soobshcheniya Gosudarstvennogo Naicho-issledovatel' nogo Proektnogo Instituta Azotnoi Promyshlennosti Produktivnykh Organov Sinteza; (24); 74-79 (1969)

LUENGO, C.A.; CABRERA, A.I.; MacKAY, H.B.; MAPLE, M.B. (1977)
Catalysis of carbon monoxide and carbon dioxide methanation by cerium-aluminium ($CeAl_2$), cerium-cobalt ($CeCo_2$), Cerium-nickel ($CeNi_2$), cobalt and nickel
Journal of Catalysis; 47 (1); 1-10 (1977)

LUFT, W.; MEYE, H.; SPINDLER, H.; WRUBEL, A. (1975)
Catalyst for the reaction of hydrogen with carbon oxides to form methane
German (East) Patent; 116,450, 3pp (20 Nov 1975)

LUNDE, P.J.; KESTER, F.L. (1974)
Carbon dioxide methanation on a ruthenium catalyst
Industrial and Engineering Chemistry, Process Design and Development; 13 (1); 27-33 (Jan 1974)

MARTIN, G.A.; DALMON, J.A.; PRIMET, M. (1977)
Interaction in the 300-400 K range of carbon monoxide and hydrogen with silica-supported nickel
Comptes Rendus Hebdomadaires Séances publiques de l'Acadêmi des Sciences; Series C.,
284 (4); 163-165 (1977)

MASAGUTOV, R.M.; SEMENOVA, E.B.; CHERKASOV, R.I.; TIKHANOSKAYA, S.G. (1976)
Hydrogenation of carbon dioxide on a nickel catalyst on kieselguhr
Kinetika i Kateliz; 17 (4); 1080 (1976)

McARTHUR, D.P. (1974a)
Aluminium borate catalyst compositions.
US Patent 3,856,702; 10 pp (24 Dec 1974)

McARTHUR, D.P. (1974b)
Aluminium borate catalyst compositions
US Patent 3,856,705 10pp (24 Dec 1974)

McARTHUR, D.P. (1977a)
Aluminium borate catalyst compositions and use
US Patent 4,024,171; 10pp (17 May 1977)

McARTHUR, D.P. (1977b)
Thermally stable nickel-alumina catalysts useful for methanation and other reactions
US Patent 4,042,532; 6pp (16 Aug 1977)

McARTHUR, D.P. (1977c)
Thermally stable nickel-aluminium catalysts useful for methanation
US Patent 4,064,152; 6 pp (20 Dec 1977)

MILLS, G.A.; STEFFGEN, F.W. (1973)
Catalytic methanation
Catalysis Reviews, Science and Engineering: 8 (2); 159-210 (1973)

MITCHELL, R.W.; PANDOLFI, L.J.; MAYBURY, P.C. (1976)
$(Co_2B)_{10}RhH_6$ and $(Ni_2B)_{10}$ RhH_{15} as versatile catalysts for hydrogenation, hydrogenolysis, and methanation reactions
Journal of the Chemical Society, Chemical Communications; (5); 172-173 (1976)

MITCHELL, T.O.; WHITEHURST, D.D. (1977)
Synthetic amorphous silicas of pre-determined pore distribution
US Patent 4,003,825; 10 pp (18 Jan 1977)

MOELLER, F.W.; HEINZ, J. (1976)
Methane production
German Patent 2, 436, 297; 8 pp (29 Jan 1976)

MOELLER, F.W.; MUELLER, W.D.; HEIDL, H. (1976)
Gas interchangeable with natural gas
Canadian Patent 985,048; 18 pp (9 Mar 1976)

MOHNOT, S.; KYLE, B.G. (1978)
Equilibrium gas-phase compositions and carbon deposition boundaries in the CHO-inert system
Industrial and Engineering Chemistry, Process Design and Development; 17(3); 270-272 (1978)

MOLDOVAN, A.G.; ELATTAR, A.; WALLACE, W.E. (1978)
Studies of the methanation catalysts thorium-nickel ($ThNi_5$) and zirconium-nickel ($ZrNi_5$) by Auger and characteristic energy loss spectra
Journal of Solid State Chemistry; 25 (1); 23-29 (1978)

MORITA, Y.; KIKUCHI, E.; INO, T. (1977)
High-caloric value fuel gas
Japanese Patent 77 16,501; 5 pp (7 Feb. 1977)

MULAY, L.N.; EVERSON, R.C.; MAHAJAN, O.P.; WALKER, P.L. (1976)
Magnetic characteristics of amorphous nickel catalysts and their methanation activity
In: *Proceedings 21st Annual Conference on Magnetism and Magnetic Materials,* Philadelphia, PA, 9–12 Dec, 1975, New York, American Institute of Physics, 536-537 (1976)

NOVOHRADSKY, M. (1960)
Synteza methanu z vodiku a kyslicniku uhelnatelho popripade uhliciteho
Ustav Pro Vyzkum Paliv, Prace; 1; 153-157 (1960)

NOZAWA, I.; SHIRASAKI, T. (1978)
Structure, reducibility, and catalytic activity of supported nickel oxide catalysts. I. Reducibility of supported nickel oxide catalysts
Nippon Kagaku Kaishi; (8); 1062 – 1065 (1978)

ODEN, L.L.; RUSSELL, J.H. (1978)
Methanation activity of Raney nickel catalysts. Effects of proportion of nickel-aluminium ($NiAl_3$ *and* Ni_2Al_3) *in precursor alloys*
US Bureau of Mines, Report of Investigations RI8272, 15 pp (1978)

ODEN, L.L.; SANKER, P.E.; RUSSELL, J.H. (1976)
Preparing supported Raney nickel catalysts by dip coating
US Bureau of Mines, Report of Investigations, RI8184, PB-261 415 13 pp (Oct 1976)
Albany, Oreg., Bureau of Mines

O'HARE, S.A.; MAUSER, J.E.; ARMENTROUT, C.E. (1976)
Massive catalytic inserts
US Patent Application 709,999; 10 pp (30 Jul 1976)

O'HARE, S.A.; MAUSER, J.E.; ARMANTROUT, C.E. (1977)
Massive catalyst
US Patent Application 796,639; 11 pp (13 May 1977)

PARTHASARATHY, R. (1976)
Methanation catalyst.
US Patent 3,933,883; 4 pp (20 Jan 1976)

PONEC. V. (1978)
Some aspects of the mechanism of methanation and Fischer-Tropsch synthesis
Catalysis Reviews – Science and Engineering; 18(1); 151-171 (1978)

POP, G.; MIHAI, A.; NICOLESCU, I.; ANGELESCU, E.; IONITA, V.; PARAUSANU, V.; DARDAN, M. (1971)
Catalyst for the conversion of carbon monoxide into methane
Romanian Patent 53,011, 3 pp (2 Dec. 1971)

QUACH, T.Q.P. (1976)
Kinetics of the reaction between carbon dioxide and hydrogen over a ruthenium catalyst in a continuous stirred tank reactor
Journal of Applied Chemistry and Biotechnology; 26 (10); 527-535 (1976)

RABO, J.A.; RISCH, A.P.; POUTSMA, M.L. (1978)
Reactions of carbon monoxide and hydrogen on cobalt, nickel, ruthenium and palladium metals
Journal of Catalysis; 53(3); 295-311 (Jul 1978)

RANDHAVA, S.S. (1972)
Selected catalytic methanation of a gaseous mixture containing carbon monoxide
US Patent 3,663,162; 5 pp (16 May 1972)

RANDHAVA, S.S.; REHMAT, A. (1970)
Hydrogenation of carbon dioxide in ppm levels
American Chemical Society, Division of Fuel Chemistry, Preprints;
14 (3); 1-9 (1970)

RANDHAVA, S.S.; REHMAT, A.; CAMARA, E.H. (1969 a)
Methanation of low concentration carbon monoxide feeds over ruthenium
Industrial and Engineering Chemistry, Process Design and Development;
8 (4); 482-486 (Oct 1969)

RANDHAVA, S.S.; CAMARA, E.H.; REHMAT, A. (1969b)
Methanation of low levels of carbon monoxide over a nickel catalyst
Industrial and Engineering Chemistry, Product Research and Development;
8 (4); 347-351 (Dec 1969).

REDDY, M.R.; GEANANGEL, R.A.; WENDLANDT, W.W. (1978)
Nickel molybdate ($NiMoO_4$) as methanation catalysts
Thermochimica Acta, 25 (1); 117-121 (1978)

REHMAT, A.; RANDHAVA, S.S. (1970)
Methanation of carbon monoxide
Industrial and Engineering Chemistry, Product Research and Development 9 (4); 512-515 (Dec 1970)

ROBINSON, H.E. (1973)
Layered complex metal silicate compositions and their preparation
US Patent 3,729,429; 20 pp (24 Apr 1973).

ROTTIG, W.; SCHENK, K. (1955)
Process for the methanisation of gas mixtures containing oxides of carbon and hydrogen
German Patent 933, 803; 3 pp (8 Sep 1955)

ROTTIG, W. (1962)
Process for the methanisation of gas mixtures containing essentially only carbon dioxide and hydrogen
German Patent 1, 110 147; 3 pp (18 Jan 1962)

RUDAJEVOVA, A.; POUR, V. (1975)
Determination of the surface area of nickel in a nickel/aluminium oxide catalyst using the method of chemisorption and of magnetization changes
Collection of Czechoslovak Chemical Communications; 40 (4); 1126-1134 (1975)

RUHRCHEMIE, A.G. (1957)
Process for the purification and methanisation of gas mixtures containing oxides of carbon and hydrogen
British Patent 774, 283; 6 pp (8 May 1957)

RUSSELL, J.H.; ODEN, L.L.; SANKER, P.E. (1977)
Temperature control of supported catalysts
U.S. Patent Application 778, 272; 13 pp (16 Mar 1977)

SABATIER, P.; SENDERENS, J.B. (1902)
Nouvelles syntheses du methane (New Syntheses of Methane)
Comptes Rendus de l'Académie des Sciences, Paris; 134; 514 (1902)

SABATIER, P.; SENDERENS, J.B. (1905)
New general methods of hydrogenation and of molecular reactions based on the use of finely divided metals
Journal of the Chemical Society; Abstracts of Papers on Organic Chemistry; 88 (1); 333 (1905)

SACHTLER, J.W.A.; KOOL, J.M.; PONEC, V. (1979)
The role of carbon in methanation on cobalt and ruthenium
Journal of Catalysis; 56, 284-286 (1979)

SANKER, P.E.; ODEN, L.L.; RUSSELL, J.H. (1976)
Supported Raney-type catalysts by reactive diffusion
U.S. Patent Application 709, 990; 11 pp (30 Jul 1976)

SAPPER, E.; LAURER, P.R. (1978)
Supported nickel catalyst
German Patent 2,716,933; 6 pp (9 Feb 1978)

SCHEHL, R.R.; PENNLINE, H.N.; STRAKEY, J.P.; HAYNES, W.P. (1976)
Pilot plant operation of a non-adriabatic methanation reactor
American Chemical Society, Division of Fuel Chemistry, Preprints of papers presented at San Francisco, 29 Aug–3 Sep 1976, 21 (4); (1976)

SCHISHKOVA, V.N. and others (1970)
Method of cleaning hydrogen containing gas mixtures of oxygen bearing contaminants
USSR Patent 200, 102; 1 pp (29 Aug 1967)

SCHOUBYE, P. (1969)
Methanation of carbon monoxide on a nickel catalyst
Journal of Catalysis; 14 (3); 238-246 (1969)

SCHOUBYE, P. (1970)
Methanation of carbon monoxide on a nickel catalyst
Journal of Catalysis; 18 (1); 118-119 (1970)

SHALVOY, R.B.; REUCROFT, P.J. (1977)
Quantitative analysis of ESCA signal intensities from coprecipitated nickel on alumina catalysts
Journal of Electron Spectroscopy and Related Phenomena; 12 (3); 351-356 (1977)

SHERWIN, M.B.; FRANK, M.E.; BLUM, D.B. (1975)
Progress in liquid phase methanation
In: *Proceedings of the Seventh Synthetic Pipeline Gas Symposium*
Chicago, Ill., Oct 1975, 297-308 (1975)

SIDEL'NIKOV, I.I.; MARTYUSHIN, E.I.; NIKITINA, L.N. (1976)
Mathematical description of methane conversion in a fluidized bed of catalyst in apparatus of ring cross section
From: *Chemical Abstracts;* 85, 163068x (1976)

SLAUGH, L.H. (1976)
Methanation Catalyst
US Patent 3,996,256; 4 pp (7 Dec 1976)

SOKOL, L.; KREJCI, V.; UHLIR, J.; HOUBY, A. (1970)
Purification of a nitrogen-hydrogen mixture by methanation of carbon monoxide and carbon dioxide. III. Improvement of methanation apparatus
Sbornik Praci Vyzkumie Chemikeho Vyuziti Uhli, Dehtukopy; (10); 129-137 (1970)

SOLO, M. (1962)
Kinetics of the hydrogenation of carbon dioxide over a nickel-chromium oxide catalyst
Collection of Czechoslovakian Chemical Communications; 27 (11); 2621-2627 (1962)

STAEGE, H.; GOEKE, E. (1975)
Methane containing gas
German Patent 2, 359, 741; 15pp. (5 Jun 1975)

STILES, A.B. (1976)
Nickel chromite catalyst
German Patent 2,528,148; 30 pp (15 Jan 1976)

STORCH, H.H.; GOLUMBIC, H.; ANDERSEN, R.B. (1951)
The Fischer-Tropsch and related syntheses
New York, Wiley, xii; 610 pp (1951)

SUMMERS, J.C.; AUSEN, S.A. (1978)
Catalyst impregnation. Reactions of noble metal complexes with alumina
Journal of Catalysis; 52 (3); 445-452 (1978)

TAJBL, G.D. (1975)
Methanation process utilising split cold gas recycle
US Patent Application 538, 061; 15pp. (2 Jan 1975)

TAKENAKA, S.; YOKOTA, N.; KOBAYASHI, N.; KIMURA, O.; MATSUOKA, S. (1977)
Methanization of low-caloric gas
Japanese Patent 77 03, 643 6 pp (29 Jan 1977)

THOMAS, M.G.; BEIER, B.F.; MUETTERTIES, E.L. (1976)
Metal clusters in catalysis. IV. Catalytic hydrogen reduction of carbon monoxide to alkanes
Journal of the American Chemical Society; 98 (5), 1296-1297 (May 1976)

THOMPSON, B.H. (1971)
Catalytic production of methane-containing gases
US Patent 3,625,665; 5 pp (7 Dec 1971)

TOMII, T.; KANEKO, S. (1976)
Catalysts for methane formation from carbon oxides and hydrogen
Japanese Patent 76 70, 704; 4 pp (18 June 1976)

TOPSOE, H. (1976)
Catalyst for accelerating methanation reactions
German Patent 2, 624, 396; 21 pp (16 Dec 1976)

TRIMM, D.L. (1977)
The formation and removal of coke from nickel catalysts
Catalysis Reviews – Science and Engineering; 16 (2); 155-189 (1977)

VAHALA, J. (1971a)
Methanation catalysts. I. Effect of precipitation conditions on the properties of nickel-chromium catalysts
Chemicky-Prumiysl; 21 (2); 61-67 (1971)

VAHALA, J. (1971b)
Methanation catalysts. III Thermally stable catalysts
Chemicky Prumiysl; 21 (6); 270-277 (1971)

VAHALA, J.; JADERNIK, P. (1971)
Methanation catalysts. II. Effect of reduction, passivation and pelletization on the properties of nickel-chromium catalysts
Chemický Průmiysl, 21 (3); 97-101 (1971)

VAHALA, J.; JANECK, F. (1974)
Methanation catalyst
Czechoslavakian Patent 155,829; 2 pp (15 Nov 1974)

VAN BARNEVELD, W.A.A.; PONEC, V. (1978)
Influence of alloying on the selectivity in Fischer-Tropsch synthesis by nickel-copper alloys
Journal of Catalysis; 51 (3); 426-430 (1978)

VAN DIJK, W.L.; GROENEWEGAN, J.A.; PONEC, V. (1976)
The dissociative adsorption of carbon monoxide on nickel and nickel-copper alloys
Journal of Catalysis; 45(2); 277-280 (Nov 1976)

VAN HERWIJNEN, T.; VAN DOESBURG, H.; DE JONG, W.A. (1973)
Kinetics of the methanation of carbon monoxide and carbon dioxide on a nickel catalyst
Journal of Catalysis; 28 (3); 391-402 (1973)

VANNICE, M.A. (1975a)
Catalytic synthesis of hydrocarbons from hydrogen-carbon monoxide mixtures over the Group VIII metals. I. Specific activities and product distributions of supported metals
Journal of Catalysis; 37 (3); 449-461 (1975)

VANNICE, M.A. (1975b)
Catalytic synthesis of hydrocarbons from hydrogen-carbon monoxide mixtures over the Group VIII metals. II. Kinetics of the methanation reaction over supported metals
Journal of Catalysis; 37 (3); 462-473 (1975)

VANNICE, M.A. (1976a)
Synthesis of hydrocarbons from carbon monoxide and hydrogen
Catalysis Reviews, Science and Engineering; 14 (2); 154-191 (1976)

VANNICE, M.A. (1976b)
The catalytic synthesis of hydrocarbons from hydrogen-carbon monoxide mixtures over the Group VIII metals. IV. The kinetic behaviour of carbon monoxide hydrogenation over nickel catalysts
Journal of Catalysis; 44 (1); 152-162 (1976)

VANNICE, M.A. (1977)
Catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen
Advances in Chemistry Series; 163; 15-32 (1977)

VEROSTKO, C.E.; FORSYTHE, R.K. (1974)
Study of the Sabatier methanation reaction kinetics
Society of Automobile Engineers
Preprint 740 933 for Meeting 29 Jul – 1 Aug 1974, 52 pp

VLASENKO, V.M.; YUZEFOVICH, G.E. (1969)
Mechanism of the catalytic hydrogenation of carbon oxides to methane
Uspekhi Khimii; 39 (9) 1622-1643 (1969)

VOGT, W.; KOCH, J.; GLASER, H. (1978)
Catalyst for the reduction of carbon monoxide with hydrogen
German Patent 2,653,985; 16 pp (1 June 1978)

WALLACE, W.E.; ELATTAR, A.; TAKESHITA, T.; COON, V.; BECHMAN, C.A.; CRAIG, R.S. (1977)
Rare earth and actinide intermetallics as catalysts
In: *Proceedings of the Second International Conference on the Electronic Structure of Actinides,*
Wroclaw, Poland, Sep. 1976, 357-365 (1977).

WENDLANDT, R.; HOFFMAN, G. (1958)
Catalytic manufacture of methane-containing mixtures from carbon monoxide and hydrogen
German Patent 970, 913; 5 pp (Nov 13 1958)

WENDLANDT, R.; HOFFMAN, G.; KOKERT, E. (1954)
Methane from carbon monoxide and hydrogen
British Patent; 705, 623; 6 pp (17 Mar 1954)

WENKE, K. (1958)
Investigations into the catalytic production of methane from mixtures of carbon monoxide and hydrogen
Journal für Praktische Chemie, Series 4; 6 (3-4); 204-224 (Jul 1958)

WENTRECEK, P.R.; McCARTY, J.G.; WOOD, B.J.; WISE, H. (1976a)
Formation of surface carbon and methanation catalysis on alumina supported nickel
American Chemical Society, Division of Fuel Chemistry Preprints; 21 (4); 52-63 (1976)

WENTRCEK, P.R.; WOOD, B.J.; WISE, H. (1976b)
The role of surface carbon in catalytic methanation
Journal of Catalysis; 43 (1-3); 363-366 (1976)

WHITE, G.A.; ROSZKOWSKI, T.R. (1976)
Substitute natural gas
U.S. Patent 3, 938, 968; 30 pp (17 Feb 1976)

WHITE, G.A.; ROSZKOWSKI, T.R.; STANBRIDGE, D.W. (1975)
Predict carbon formation
Hydrocarbon Processing; 54(7); 130-136 (Jul 1975)

WOODWARD, C. (1975)
Catalyst precursor and its reaction product used in methane formation
German Parent 2,621, 314; 35 pp (18 Nov 1976) (British Appl. 75/20, 621. 15 May 1975. 35 pp.)

YATES, J.T.; GOODMAN, D.W.; MADEY, T.E. (1977)
Decomposition of formaldehyde and methanol on ruthenium and nickel
Proceedings of the Seventh International Vacuum Congress,
Vienna, 12-16 Sep 1977; 2; 1133-1136 (1977)

ZLOBINA, M.P.; CHESNOKOVA, R.B.; ALEKSEEV, A.M.; LYUDKOVSKAYA, B.G.; VOLYNKINA, A. Ya.; D'YAKONOV, Ya.I; EGEUBAEV, S.Kh. (1973)
Effect of various factors on the calcination of nickel aluminium methanation catalysts
Trudy Gosudarstvennogo Naucho -issledovatel'nogo proektnogo Instituta Azotnoi Promyshlennosti Organov Sinteza; 19; 45-51 (1973)

Reproduced by NTIS

National Technical Information Service
Springfield, VA 22161

This report was printed specifically for your order from nearly 3 million titles available in our collection.

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

About NTIS

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at http://www.ntis.gov.

NTIS

Ensuring Permanent, Easy Access to U.S. Government Information Assets

SATISFACTION GUARANTEED

NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.

▶E-mail: info@ntis.gov
▶Phone: 1-888-584-8332 or (703)605-6050

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000