CHAPTER 2

THEORY OF METHANOL SYNTHESIS

2.1 Literature Survey on Methanol Synthesis

Methanol could be synthesized in many ways from different raw materials, in the presence of various catalysts and under different reaction.

In terms of raw material, it might be said that synthesis gas consisting of CO and H_2 was technically the most appropriate to manufacture methanol. De Oliveira, Eduardo Sabins (1979) prepared synthesis gas for methanol manufacture by passing steam over C at $> 500^{\circ}C$. **Heat** was supplied by passing an electrical current through the C or by combustion of auxiliary fuel, from which waste heat was recovered. Syngas was obtained by Diemer and et al (1981) from partial oxidation of coke-oven gas (CG) with O or O-enriched air at 1,100-1,600°C. Partial oxidation was proceeded by first cooling the CG to $< 70^{\circ}C$ for the removal of tar down to a residual content of 1-5 g tar/m^3 CG and secondly by the removal of dust and H_2S. Then, tar-free CG containing H 59, CH_4 23.6, C_nH_m 3.4, N 4.7, CO 5.5, CO_2 2, O 0.3, and others 1.5 vol % was subjected to partial oxidation at 1.04 bar and 1,300°C by the addition of 0.3 m^3 O/m^3 CG and 0.03 kg H_2O/m^3 CG. The partially oxidized CG containing CO_2 2.6, CO 27.4, H 65.5, N + Ar 4.1, and H_2S + COS 0.4 vol % was purified in an electrostatic precipitator for the removal of dust and treated, with methanol at -30 to -40°C for the removal of S compounds. The dust-free and S-free synthesis gas was compressed to 50-80 bar and used for the catalytic synthesis of methanol. The spent methanol was regenerated and the liberated H_2S used for preparation of elemental S by the Claus process.

2.1.1 Survey on metal-oxide catalysts

Catalysts used for methanol synthesis were both homogeneous and heterogeneous. Most heterogeneous catalysts were either pure CuO, ZnO, Cr_2O_3, MnO and Al_2O_3, or binary, ternary and quarternary mixtures of these. Homogeneous catalysts were mostly transition metals, such as Rh, Pd and Ru.

Mitsushima et al (1969) studied the effects of aluminium oxide addition to copper-zinc oxide catalyst on methanol synthesis by keeping the ratio of Cu to Zn constant and varying the content of Al_2O_3. The catalyti activity was measured at a space velocity of 10,000 hr^{-1}, pressure of 60 kg/cm^2 and 200-350°C. It was found that the ratio of surface area of exposed Cu to the total surface area of the catalyst had a maximum at 10% Al content and catalytic activity was also maximum at this composition.

The effect of depositing copper on the surface of a reduced Zn-Cr catalyst was studied by Vlasenko and et al (1969), Wang Ching and et al. (1982) found that samples containing 8.6 % Cu had the highest selectivity and good stability, the selectivity remaining almost constant for more than 90 hours.

Zinc-chromium-copper catalyst was prepared by Kravchenko, F.F. and et al. (1968) for synthesizing methanol by mixing a compound of Cu with ZnO, chromium acid and promoters, with subsequent drying and formation of catalyst. A basic Cu chromate was used as the original Cu compound.

Properties and structure of a mixed catalyst from basic copper carbonate and zinc carbonate was studied by Terao and et al. (1968). A correlation between activity and structure of the calcined CuO-ZnO mixed catalysts was examined with respect to methanol synthesis. The methanol yield was determined chromatographically and the structure was determined X-ray photographically (Cu-K_α-radiation) CO adsorption was also examined. The activity (κ) was found to depend on the Cu surface area (S_{cu}). Heat resistance of the catalysts increased with a greater $\kappa/_{S_{cu}}$ ratio. The difference in catalytic activity in methanol synthesis were attributed to the different sizes of CuO and ZnO nuclei as well as to different relative sizes of CuO and ZnO nucli and to different concentrations of CuO and ZnO in the mixture.

Sopava et al (1970) produced $ZnCrO_4$-2.5 ZnO catalysts from Cr and Zn oxides coprecipitated from a solution of their nitrates and found that it had optimum mechanical strength and selectivity in the synthesis at 280 atm and 320-380°C of methanol from 2.7-2.8:1 H_2:CO mixtures introduced at a space velocity of 40,000 hr^{-1}. The 5 mm×5 mm tablets were pressed at 2600-8200 kg/cm^2 from uncalcined oxide mixtures containing 1.5 - 2.0 % added graphite and were calcined in H_2. by heating at 100°C/hr to 380°C.

A.C.P. McIntosh (1978) described briefly the conventional high pressure process (about 350 bars) and the success of the newer ICI low pressure process, which used a copper based catalyst in place of the zinc oxide-chromium trioxide catalysts used in high pressure-high temperature plants. The ICI low pressure process allowed operation at a lower temperature and at pressure as low as 50 bars. It also resulted in simplification of plant design and operation, and substantial reduction in energy consumption.

M.S. Wainwright (1978) presented preliminary results of an investigation into the use of Raney copper catalysts promoted with zinc and chromium for synthesis of methanol from carbon monoxide and hydrogen. Physical and chemical properties of the Raney copper had been investicated using a wide range of analytical techniques. The potential of using promoted Raney copper to catalyze the reaction and possible reaction mechanism were also dicussed.

Cornthwaite, Derek (1970) prepared methanol synthesis catalysts from Cu oxide and mixed oxides of spinel structure. The catalyst pellets might also contain ZnO, Al_2O_3 or Na_2O or a combination of these oxides. These catalysts served to exemplify reductive catalysts. Temperature for the reaction ranged from 190-270°C and 10-150 atm, typically 80-120 atm. Combination of various reaction conditions with the improved nature of the catalysts provided for a more efficient formation of synthetic methanol.

Il'ko, E.G. et al (1982) prepared the catalysts $2CuO.ZnO.0.08Cr_2O_3$, 2CuO.ZnO, $2CuO.ZnO.0.16Cr_2O_3$, $2CuO.ZnO.0.25Cr_2O_3$, and $0.5CuO.ZnO.0.25Cr_2O_3$ by coprecipiting Cu and Zn carbonates, adding stabilizing additives (6% Al_2O_3 or 3% MgO), drying, baking, and tablet compression. Initially, metallic Cu (or Zn) was dissolved as in : $2Cu + O_2 + nNH_3 + 2CO_2 \rightarrow 2[Cu(NH_3)_n]CO_3$ where n = 2-4. Al_2O_3 was formed in situ from Al formate. Precipitation $NH_3 + CO_2$ did not form the alkali metal waste in the wastewater that was formed by the conventional precipitation method using alkali metal carbonates. Catalysts thus prepared exhibited activity of the same intensity as catalysts prepared by using other methods.

Men'shova et al. (1983) prepared catalysts that composed of Cu, Zn, Al, and Cr oxides by combining the thermolysis and reduction steps. The catalysts were highly active in methanol synthesis from synthesis gas.

Bridgewater et al. (1983) studied methanol synthesis over Raney Cu catalysts made by selectively leaching Al and Zn from Al-Cu-Zn alloys with aqueous NaOH. The methanol yields exceeded those obtained with an industrial catalyst. Catalysts made from alloys containing the ternary phase Cu_3Al_3Zn had the highest specific activity but developed low surface areas due to the resistance to leaching of Al and Zn. Synergism was observed between Raney Cu and Zn oxide reprecipitated during extraction. The Cu was probably present as Cu^0 under methanol synthesis conditions.

Kotoski et al (1978) prepared a methanol synthesis, or CO conversion, catalyst by washing the precipitant of CuO to the neutral state, drying, mixing with graphite and granulating using $HReO_4$ or NH_4ReO_4 solutions. The obtained granules were compressed to tablets. More specifically, an aqueous solution of $Cu(NO_3)_2.3H_2O + Zn(NO_3)_2.6H_2O + Al(NO_3)_3.9H_2O$ was heated to 90-100°C and mixed with 90-100°C Na_2CO_3. The precipitant was washed to neutral, dried at 110°C and then 300°C, and then treated with an aqueous solution of NH_4ReO_4.

Lender et al. (1982) reported that in the synthesis of methanol over SNM-1 catalyst the rate of diffusion of methanol was the limiting factor. The reaction rate did not depend on the diameter (5x5 vs. 9x9 mm) of the catalyst granules.

Friedrich et al. (1982) developed a Raney-type low temperature methanol synthesis catalyst. Catalysts prepared by caustic leaching of Cu-Zn-Al alloys had activities greater than that of a composed Cu-based catalyst. The most active catalyst for methanol synthesis was prepared from alloys containing 10-20% Zn and ~50% Al. The activity of the catalysts depended on the leaching time.

2.1.2 Survey on Rare-Earth Metal Catalysts for MeOH Synthesis

Methanol synthesis catalysts mentioned in 2.1.1 as well as decomposition catalysts in 2.1.3 mostly consist of Cu, Zn, Cr, Na, Mg, etc.. The following catalysts are mostly composed of rare-earth metals, such as Rh, Pt, Pd, In etc. and are either homogeneous or heterogeneous catalysts.

Mitsui Taotsu Chemicals, Inc. (1981) prepared methanol by hydrogenating CO or CO_2 in the presence of Cu, Pd, Pt or their oxide in an alkali slurry. Autoclaving a slurry prepared from 2.0 g Pd powder, 150 ml H_2O, and 600 mg NaOH with CO-H (molar ratio 1.0 ; 270 kg/cm^2) at 220°C and 395 kg/cm^2 for 6 hours gave 0.53 g methanol with traces of ethanol and MeCHO.

Pruett et al. (1982) found that the cluster compounds $(RCN)_2M_2Ru_6C(CO)_{16}$ (R = C_{1-16} alkyl, Ph, or C_{6-10} aralkyl ; M = Cu, Ag, or Au) were useful as homogeneous catalysts for converting synthsis gas to methanol. For example, $(Et_4N^+)_2\ Ru_6C(CO)_{16}^{\ 2-}$ in acetone was added to $Cu(MeCN)_4^+\ BF_4^-$ in acetone to make $(MeCN)_2Cu_2R_6(CO)_{16}$, which was added (0.6 g) along with 200 ml THF to a reactor. The reactor was then charged with synthesis gas and heated to 275°C, 120 MPa for 5 hours to yield 17g methanol, 3.8g HCO_2Me and no hydrocarbons.

Sumitomo Chemical Co. Ltd. (1982) found that in the preparation of MeOH and/or Me_2O from CO and H, a mixture of Pd and a metal selected from Group Ia or Group IIa on catalyst carriers were used as catalysts. Thus, $Na_2(PdCL_4)$ aqueous solution was mixed with AL_2O_3, dried 5 h at 120° and reduced by H 2 h at 300° to give catalyst. CO and H (1:2 ratio) were passed over the catalyst at 180°C to give MeOH and Me_2O (combined selectivity was 91%)

Dombek (1981) prepared $HOCH_2CH_2OH$,EtOH, and MEOH in the liquid phase from CO and H in the presence of a Ru carbonyl complex with IR bands at 2100 ± 10 cm^{-1}, 2015 ± 10 cm^{-1}, and 1990 ± 10 cm^{-1}, at 50-400°C and 500-1500 psi. H-CO (1:1) was treated with $(Ph_3P)_2N[Ru(CO)_3I_3]$ and 2 equivalent $(Ph_3P_2N)\left[HRu_3(CO)_{11}\right]$ in the presence of NaI at 12500 psi and 230°C to give MeOH 2.92 and $HOCH_2CH_2OH$ 0.41 mol hr^{-1}

Lin, Jiang Jen (1982) prepared alkonols especially MeOH, with high selectivity from a CO-H mixture at ⩾150° and ⩾ 500 psig in 1, 4 - dioxane or a similar solvent over a catalyst system comprising a Ru compound., a Re or Mn compound, a quaternary phosphonium or ammonium compound, and in some cases, Ph_3P. For example, a 1:1 (molar) CO-H mixture was added at 220°C/8100 psi to a reactor containing 10 ml 1, 4-dioxane, 0.19 g hydrated RuO_2, 3.4 g Bu_4PBr, and 84 mg $Mn_2(CO)_{10}$. After 16 hours, the solvent contained 4.0 g reaction products containing 3.2 g MeOH and 0.24 g EtOH.

Sumitomo Chemical Co.Ltd.(1984) carried out the manufacturing oxygen-containing hydrocarbons from carbon monoxide and hydrogen process with improved selectivity for MeOH and EtOH in the presence of a supported Group VIII metal catalyst containing cocatalyst(s) chosen from alkali metals and Tl. For example, 4.0 g $RhCl_3.2H_2O$ in 400 ml water was stirred with 35% HCl 5.1, K_2CO_3 6.7g, and γ-Al_2O_3 38.6 g for 1 hour, concd., and dried at 120° for 5 h to give a catalyst. The catalyst (1 g) was reduced with 40 ml/min H for 6 h at 220°C, placed in an autoclave under N, pressured with 1:1 CO-H to 40 kg/cm^2, and heated at 220°C for 6 hours to give MeOH 0.809, EtOH 0.071, PrOH 0.007, BuOH trace, CO_2 0.061, CH_4 0.018, and C_2^+ hydrocarbons 0.020 mmol/g catalyst ; and selectivity for O-containing hydrocarbons was ,90.0 %, compared with 0.071, 0.014, 0.005, 0.002, 0.005, 0.248, 0.256, and 6.9, respectively in the presence of a similar catalyst prepared without K_2CO_3 and HCL.

Mitsui Petrochemical Industries, Ltd. (1982) prepared a mixture of compounds, mainly MeOH from CO and H in the presence of a Cu compound (except oxide), and alkali metal alkoxide, and optionally other cocatalysts. For example, autoclaving 1 mmol CuCl, 11 mmol NaOMe, and 10 ml THF under 50-70 kg/cm^2 pressure of 3:7 (molar) CO-H at 80°C for 9 hours gave MeOH 124.5, HCO_2Me 8.8, and EtOH 0.1 mmol, while no O-containing compounds were obtained in the presence of NaOMe and only 0.26 mmol MeOH was obtained in the absence of CuCl.

Mitsui Petrochemical Industries, Ltd. (1982) studied the preparation of alkanepolyoles by hydrogenation of CO in the presence of Rh compounds and alkali iodide. The gram atom ratio of the alkali metal : Rh was 1:1 to 100 : 1. Autoclaving a mixture of Rh $(CO)_2$ acetylacetone 0.3 mmol, KI 3.7 mmol (gram atom ratio of K:Rh = 12 : 13), sulfolane 7.5 ml, and a 1:1 mixture of CO and H (200 kg/cm^2) at 240°C and 300 kg/cm^2 for 4 hours gave 0.44 ethylene glycol/hr/g Rh and 0.58 g MeOH/hr/g Rh

Mitsui Petrochemical Industries, Ltd. (1982) studied the catalyst system for hydrogenation of CO in the preparation of alkanepolyols. The catalyst system comprised Rh compounds, Ru compounds and 1 or mover compounds selected from alkali metal compounds, alkali earth metal compounds, NH_3, quaternary ammonium compounds, and organic amines. For example, autoclaving a mixture of $Rh(CO)_2$ acetylacetone 78 mg, $Ru_3(CO)_{12}$ 44 mg, KI 301 mg, sulfolane 7.5 ml and a 1 : 1 mixture of CO and H(200 kg/cm^2) at 240°C for 4 hours gave 3.85 mmol MeOH and 0.85 mmol ethylene glycol vs. 2.40 and 0.64 mmol, respectively, without $Ru_3(CO)_{12}$.

Poels et. al. (1982) prepared catalysts which, compared with catalyst containing no Mg or La compound had higher activity and selectivity to MeOH in the preparation of MeOH from synthesis gas. Silica was impregnated with $PdCl_2$, $Mg(NO_3)_2$, or La_2O_3 and reduced in H at 575K. Several method of Pd^{n+} by acetylacetone, spectrometry, SEM, etc.) indicated that Mg and La promoted the formation and stabilization of positive centers Pd^{n+}, which are essential for the preparation of methanol from synthesis gas.

Fattore et. al. (1983) prepared catalysts for the preparation of alcohols from H and CO, which had the composition $ZnCr_aCu_bA_cM_dO_x$, where A = alkali metal, M = other metal, a = 0.1-0.8, b = 0.005-0.05 ; c = 0.002-0.2, d = 0-0.1, x as required. For instance, a mixture containing 66-69% H and 30-33% CO was passed over a catalyst of composition $ZnCr_{0.3}Cu_{0.027}K_{0.02}O_x$ at 398-404°C/900 kPa to give a product containing 57.7 MeOH, 1.9 EtOH, 1.5 PrOH, 18.1 Me_2CHCH_2OH, and 21.5 wt% C_5+ alcohols.

Lisitsyn et. al. (1983) described catalysts for preparation of alcohols by hydrogenation of CO. The catalysts comprised a $Co_2(CO)_8$

or $HFeCo_3(CO)_{12}$ applied to silica gel supports, surface of which was modified with Ti or Zr hydrides. The catalysts were prepared by depositing Ti of Zr tetrabenzyl complex on silica gel, followed by decomposition of complexes in H_2 at 430°K, chemisorption of Co carbonyls, and calcination at 530 K. The catalysts provided 5-30% yield of MeOH and EtOH.

Dombek et. al (1983) prepared alcohols, especially $HOCH_2CH_2OH$ and MeOH from CO-H by homogeneous catalysis using solubilized Ru carbonyls and Rh carbonyls promoted by alkali metal halides or acetates. For instance, CO-H was added to 75 ml N-methylpyrrolidinone containing NaI 18, $Ru_3(CO)_{12}$ 6, and $Rh(CO)_2$ 3 mmol at 230°C/862.5 bar and $HOCH_2CH_2OH$ and MeOH were obtained at rates of 2.89 and 3.45 mol/l/h, respectively.

Agency of Industrial Sciences and Technology (1983) prepared alkanediols by reaction of CO with H in the presence of catalysts comprising Ru compounds, amines, and halides. A mixture of 0.3 mg-atom $Ru_3(CO)_{12}$, 1.8 mmol CsI, 1.5 mmol imidazole, and 200 kg/cm^2 1:1 M CO-H in sulfolane was autoclaved for 4 hours at 200°C to give 0.78 mmol $(CH_2OH)_2$ and 2.63 mmol MeOH.

Dombek (1983) converted CO and H into MeOH, $HOCH_2CH_2OH$, and EtOH using halide-promoted Ru catalysts in organic solvents. Iodine salts were exceptionally good promoters for this system. Spectroscopic and reaction studies showed that 2 Ru complexes, $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$ were present during catalysis and were essential for optimum activity. The roles of these complexes in catalysis were also discussed.

Vidal (1982) found that reaction of Rh(CO)$_2$(CH(COMe)) 3.1304 g with CsOBz 0.7096 g in 18-crown-6 (L) gave the (CsL)+ salt of $(Rh_{22}(CO)_{35}H_x)^{n-}$ (I ; x = 0-10, n = 0-5 etc.). I was used as a catalyst for the preparation of alcohols such as MeOH and $HOCH_2CH_2OH$ from CO and H.

Burmaster and Carter (1983) found that hollow-fiber separators (PRISM) provided steady recovery of ~60% H and ~50% CO_2 from MeOH synthesis-loop purge stream. This increased the output by 2.6-3.9% and reduced relative cost of natural gas from 91.3 to 69.8% of the total cost of operation when an 8-separator skid was used at 600 psi differential pressure. The construction of separators was described, and separator system flow diagrams and generalized material balance were given.

2.1.3 Survey on Methanol Decomposition

Per K. Frolich et al. (1928) studied the catalytic decomposition of methanol at 360°C and total pressure of 1 atm over a mixture of zinc and copper oxides in various proportion. They found that maximum decomposition of methanol and maximum formation of carbon monoxide occured when the zinc oxide was present in excess.

M.R. Fenski and Per K. Frolich (1929) studied the properties of the catalyst composed of copper, zinc, and chromium in the molal ratio of 49 : 43 : 8. They showed that this ternary mixture possessed considerably higher activity for both the decomposition and synthesis of methanol than any of the binary Cu-Zn and Cr-Zn systems. The ternary catalyst was active at low temperature, gave high conversion, and stood up well in methanol synthesis. In the decomposition experiments there was a tendency for the catalyst to deteriorate with time, but its activity might be restored by oxidation and subsequent reduction.

Robert Nussbaum, Jr., and Per K. Frolich (1931) found that a tendency toward a greater catalytic activity was indicated when the time of reduction was shortened. When added to the methanol vapor, oxygen was found to stimulate the capacity of the catalyst for decomposing methanol.

Yoon, (1981) prepared H and CO from methanol by placing methanol vapor in contact with a catalyst at 250-900°F, 0.1-50 atm absolute, for a contact time of 0.1-100 sec. Catalyst for the on-board reforming of methanol comprised Mn, Cu, and Cr. At 450, 500, and 550°F, over 50% dissociation of methanol was obtained with the Cu-Cr-Mn catalyst, rather than with the known Cu-An catalyst

2.1.4 Survey on Mechanism of MeOH Synthesis.

Susumu and Tadao (1967) studied the relative reactivity of adsorbed species during MeOH synthesis on a reduced Zn : Cr : Cu (1.0 : 0.49 : 0.16) catalyst. Abrupt changes in the ambient pressure of component in gas phase were correlated with the corresponding changes in the amounts of the adsorption and in the total ambient pressure. The results indicated that the species adsorption on the catalyst surface in a nearly equilibrated system. The simultaneous adsorption of H_2 and CO was mostly the surface intermediate complex MeO. The results were consistent with the mechanism previously proposed.

Imyanitov et. al. (1970) found that MeOH was prepared from CO and H_2 in the presence of C_2 or higher alkoxides with alkyl formates as intermediate products. CO mutual interaction was observed. The results explained in terms of displacement effect as well as enhancement effect that took place in a certain region of partial pressure. Adsorption measurement during the decomposition reaction suggested that in the initial state the adsorption species were mostly the adsorbed MeOH and that the decomposition step of MeOH was the rate determining step of the overall reaction. The mechanism of MeOH synthesis over Zinc-Oxide probable proceeds in a similar way as on the 3-component catalyst previously used.

Davydov et. al. (1983) found that the hydrogenation of CO on Pt/ Al_2O_3 catalyst at 200-500°C gave CH_4, while at temperature below 200°C MeOH was formed. The mechanism of CO hydrogenation involved its adsorption, formation of "surface carbonyl", and hydrogenation of the immobilized CO. IR spetroscopic evidence was presented in support of this machanism.

D'Amico et. al (1983) studied the interaction of CO with the $(10\bar{1}0)$ ZnO surface by high resolution electron energy loss spectroscopy (HREELS). The results represented a successful effort to use HREELS to measure the vibration of CO on any single crystal metal oxide surface and served as a complement to earlier photoelectron spectroscopic studies of the CO/ZnO system. Observation of the intraligand C-O stretching mode (273 meV, 2202 cm^{-1}) and its 1st overtone (539 meV, 4348 cm^{-1}) verified that the CO molecule adsorbed at low coverage under ultrahigh-vacuum condition on $(10\bar{1}0)$ was indeed the same high frequency CO observed on ZnO powders. In addition, observation of the Zn-C metal-ligand stretch (31 meV, 250 cm^{-1}) enabled application of a normal mode of calculation which indicated that the majority of the increased CO streching frequency was due to an increase in the CO force constant and not just due of mechanical coupling to the surface. These results were discussed in light of the mechanism of MeOH synthesis on ZnO.

2.2 Basic Knowledge of Methanol

Methanol is a clean synthetic fuel and chemical feedstock that can be made from a wide variety of material and energy sources and applied to an equally wide variety of uses. A number of factors have converged in the last few years to propel methanol to the forefront of the discusseion on synthetic fuels. The energy " crisis " of rapidly depleting petroleum resources was brought into vivid focus by the OPEC cartel's embargo of 1973. Environmental considerations have played another significant part, particularly in the difficulties of reducing automotive and power plant emissions, against which the comparative cleanliness of methanol was particularly striking. Economical factors are also of importance, with methanol providing more efficient combustion and mileage, and competing with gasoline and other synthetic fuels in predicted costs and conversion efficiency.

2.2.1 Uses

About 40% of the synthetic methanol produced today is used for the production of formaldehyde solutions including the methanol-inhibited (stabilized) grades. This use is expected to continue to grow. Formaldehyde production (86% from synthetic methanol and 14% from hydrocarbon oxidation processes as by-product) is consumed for approx 50% in resins (phenolic , urea, melamine, and acetal), 10% in urea-formaldehyde liquid concentrates, 30% in specialty chemical manufacture, and 19% miscellaneous uses. The never acetal resins, Celcon (Celanes Corp. of

America) and Delrin (E.I. du Pont de Nemours & Co., Inc.), consumed 12 million gal of formaldehyde monomer in 1965, and are continuing to expand into new uses and to supplant older resins and metals in existing uses (W.H.,1967)

The methanol antifreeze market grew steadily (except for the World War II years) to a high of 40 million gal in 1954 and thereafter declined steadily to about 8 million gal in 1965, being supplanted by the higher-boiling alcohols, principally ethylene glycol.

The use of methanol in the synthesis of methacrylates, methylamines, dimethyl terephthalate, methyl halides, ethylene glycol, and other chemicals has grown more rapidly since 1960 than other uses.

Use of methanol as an antidetonant fuel-injection fluid is declining for aircraft reciprocating and jet engines, as well as for augmented thrust in turbine engines. A minor amount is used as the principal fuel in modified engines for racing cars and boats and in miniature power plants for models.

Solvent use of methanol has increased but growth of this use is expected to taper off. It is used directly as a solvent for inks, dyes, certain resins and cements, and the manufacture of wood and metal finishes, water proofing formulations, and coated fabrics. It is also widely used as an extractant in industrial chemical processes such as refining gasoline and heating oils dewaxing dammar gum, and purifying hormones and steroids. It is also employed in numerous cleaning operations such as washing steel surfaces prior to coating, cleaning resin sheets before further processing, and in special preparations for cleaning leather and glass as well as a flusing fluid in hydraulic brade systems.

Over the past fifteen years patents and publications have been issued for many new or improved direct uses of methanol. Among these are fuel anti-icer; fuel cell component; fuel additive for rocket, jet, and combustion engine; purification of coal , coal tar, and gaseous and liquid hydrocarbons; in plastics for catalyst removal, separation, and telogenation; in metallurgy for carburization and cementation atmospheres; as a seed disingfectant; a hydraulic cement retarder; and a leaching agent for uranium ore. Countless other patents have been issued during the same period covering methanol derivatives useful in a broad spectrum of industry.

Overall a steady and substantial increase in methanol consumption seems reasonably assured.

So through the years methanol's production has been rising at a rapid rate of about 10% per annum as it has become an increasingly important chemical. (see Fig 2.1)

2.2.2 Methods of Production

Natural Methods : Extraction - Methanol can be separated or extracted from a variety of natural plants (J.P.1978). Methanol obtained during the destructive distillation of wood was the only commercial source until the introduction of the synthetic process in 1927. Hardwoods, such as birch or oak, thermally decompose when they are heated in the absence of air to temperatures of 160° to 430°C, forming charcoal, wood tar, noncondensible gases, and a watery distillate known as pyroligneous acid. Methanol , acetic acid and acetone can be extracted or distilled from this

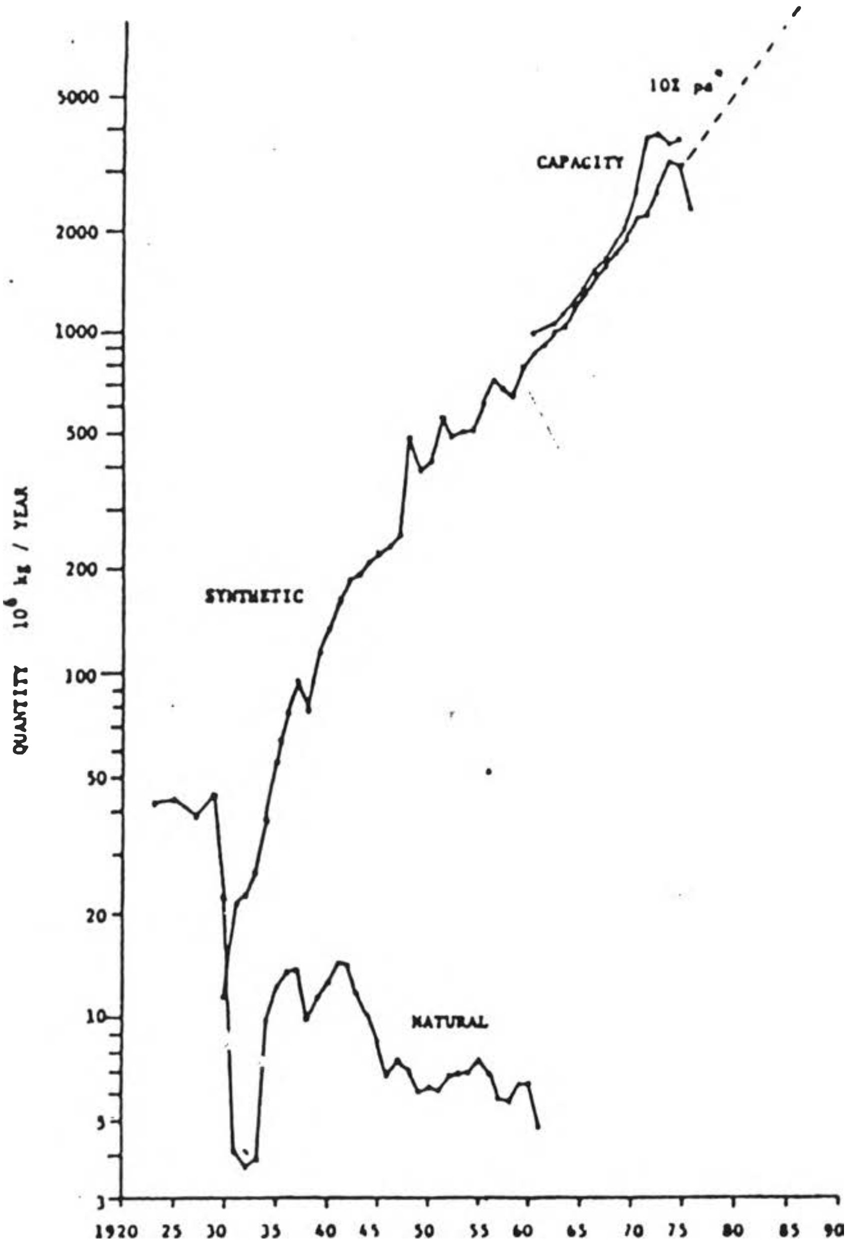


Figure 2.1 Historic Production of Methanol (J.P., 1978)

pyroligneous acid. The product is a rather crude solvent with many impurities and an offensive odor. The yield is rather small, with hardwoods giving only 1 to 2% methanol or 6 gal/ton and softwoods only half of that.

Fermentation : Methanol is found in plants and animals, and bacteria exist which can consume methanol. Thus it is conceivable that bacteria exist which could decompose the more complex natural organic materials down to methanol in a fashion analogous to the fermentation of carbohydrates to ethanol. However, no such processes are being used or apparently even know at present. This could potentially provide a convenient method of production for labor intensive areas of the world if suitable bacteria could be found or genetically engineered (J.P. 1978)

Saponification of Methyl Chloride : Manufacture of methanol from methane by way of methyl chloride is worthy of note because it constituted the first successful synthesis of the compound.

Chlorination of methane may be carried out using either chlorine or hydrogen chloride and oxygen (air), and has been the subject of numerous patents which cover catalysts and operating conditions. Other chlorination products are formed, and have to be separated. The resulting methyl chloride is saponified, for example, with caustic soda. The method never has attained commercial significance; in fact, most of the methyl chloride today is produced from methanol, instead of being used to manufacture the latter (J.P. 1978).

Low-Pressure Hydrogenation of Carbon Monoxide : Experiments have been carried out for the purpose of synthesizing methanol from carbon monoxide and hydrogen at low pressures and temperatures.

Originally conducted as a two-stage method, the process comprised action of carbon monoxide on a methanolic sodium methoxide solution (prepared by dissolving sodium metal in methanol) to yield methyl formate; conversion of methyl formate to methanol by hydrogenation in the presence of a catalyst made up, for instance, of copper, chromium, and barium oxide. The process may be represented by the following equations : (J.P. 1978)

$$H_3COH + CO \xrightarrow[30\ atm]{80^{o}C} HCOOCH_3 \tag{2.1}$$

$$HCOOCH_3 + 2H_2 \xrightarrow[30\ atm]{180^{o}C} 2CH_3OH \tag{2.2}$$

$$CO + 2H_2 \longrightarrow CH_3OH \tag{2.3}$$

The overall process may be carried out batchwise or continuously. In 1945 a pilot plant was erected. In 1954 a two-stage continuous recycle process was patented. The reaction of carbon monoxide and hydrogen is carried out in the liquid phase, for example, in a methanolic solution of sodium methoxide, and the product, methyl formate, is sent to a second hydrogenation stage where copper chromite is stated to be the preferred catalyst; the specified pressure is 20-60 atm and the temperature below 200°C, preferable between 100 and 170°C.

Methane Oxidation by Sulfur Trioxide : Some patents issued in 1948 covered the catalyzed reaction of methane and sulfur trioxide in liquid sulfuric acid at temperatures of 100-450°C and pressures up to about 1000 psi to give oxygenated and sulfonated derivatives of methane, including some methanol (W.H.,1967)

Hydrolysis of Methylal : Vapor phase continuous hydrolysis of methylal over a phosphoric acid treated charcoal catalyst at 190-285°C was patented by Newcombe. Fairly pure methanol and USP grade formaldehyde were obtained with 98% hydrolysis (W.H., 1967).

Hydration of Dimethyl Ether : In 1964 Freidlin and Matyushenskii were granted a patent by the U.S.S.R on the catalytic hydration of dimethyl ether over natural clays containing mixed metal oxides. Kruglov et al. also studied the reaction over alumina at 280-460°C.(W.H., 1967).

Synthetic Methods : From Synthesis Gas- In 1905, the French chemist Paul Sabatier suggested that methanol might be synthesized by hydrogenating carbon monoxide. M. Patart adapted the Haber process to synthesize methanol from carbon monoxide and hydrogen, and patented the process in 1921 over a temperature range of 300° to 600°C with a pressure of 150 to 200 atm. The Badische Company set up the first commercial synthetic methetic methanol plant at Leunawerke, Germany in 1923 covered by a very broad patent. They began exporting methanol to the U.S. in February 1924 at a cost of only two-thirds the existing wood-derived methanol cost.

Most methanol commercially manufactured today is made by passing a synthesis gas containing hydrogen and carbon monoxide or carbon dioxide over a catalyst under pressure and at elevated temperatures. (See equations 1,2 of Table 2 .1). Chromium and zinc or copper oxides are used as catalysts with pressures and temperatures ranging from 50 to 350 atm and up to 400°C depending on the catalysts and synthesis gas mixture. The synthesis gas has usually been formed by gasifying fossil fuels. This must be purged of all sulfur compounds to protect the synthesis catalyst. The synthesis gas is then reacted with steam in the water-gas shift reaction to shift the ratio of the gases closer to the stoichiometric ratio of 2:1 or 3:1.

Table 2.1 Reactions and Standard free Energies Relevant to Methanol Synthesis

	Reaction	G_R^o (T = °K),kJ/mol
1.	$2H_2 + CO \longrightarrow CH_3OH(g)$	$-105.0 + 0.238T$
2.	$3H_2 + CO_2 \longrightarrow CH_3OH(g) + H_2O(g)$	$-64.9 + 0.0200T$
3.	$CH_4 + SO_3 \longrightarrow CH_3OH + SO_2$	$-38.9 + 0.122T$
4.	$CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH(g)$	$-133.5 + 0.561T$
5 .	$CO + CH_3OH \longrightarrow HCOOCH_3 + H_2 \longrightarrow 2CH_3OH$	---
6.	$"CH_2" + H_2O \longrightarrow CH_3OH(g)$	$-42.3 + 0.004T$
7.	$C + H_2O(g) \longrightarrow CO + H_2$	$+133.9 - 0.141T$
8.	$C + \frac{1}{2}O_2 \longrightarrow CO$	$+110.5 - 0.089T$
9.	$CH_4 + H_2O(g) \longrightarrow CO + 3H_2$	$+215.9 - 0.234T$
10.	$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2$	$-28.5 - 0.182T$
11.	$"CH_2" + H_2O \longrightarrow CO + 2H_2$	$+147.3 - 0.234T$
12.	Coal + $O_2, H_2O \longrightarrow CO, H_2$	---
13.	Wood + $O_2, H_2O \longrightarrow CO, H_2$	---
14.	$CO + H_2O \longrightarrow CO_2 + H_2$	$40.2 + 0.037T$

The main synthesis reactions and some alternate synthesis reactions that have been proposed are given in Table 2.1. A linearized fit of the standard free energies of formation and combustion of important species in the synthesis and gasification reactions are summarized in Table 2.2.

Table 2.2 Standard Free Energies of Formation and Combustion of Species Important in Methanol Manufacture

Substance	$G_f^o(T)^{(a)}$ kJ mol^{-1}	$G_c^o(T)^{(b)}$ kJ mol^{-1}
1. $CH_3OH(g)$	-215 + 0.149T	-668 - 0.045T
2. $CH_3OH(l)$	-251 + 0.252T	-633 - 0.149T
3. $H_2O(g)$	-244 + 0.052T	0
4. $H_2O(l)$	-285 + .160T	0
5. H_2	0	-244 + 0.052T
6. CO_2	-395 + 0.0T	0
7. CO	-110 + 0.089T	-285 + 0.089T
8. C	0	-395 + 0.0T
9. CH_4	-820 + .093T	-801 + 0.011T
10. "CH_2" (c)	-13 + 0.093T	-628 + 0.041T
11. "Coal" (d)	-31	-246
12. "Wood" (e)	-48	-148
Conversion Factor: 1 cal = 4.1840J		

(a) The standard free energy of formation from the elements. Reed (J.B.,1978) fit the available data to a linear equation from $\Delta G = \Delta H - T\Delta S$ over the range 300 to 1200°K, so that the two constants in each equation are the effective vaues of ΔH_f^o and $-\Delta S_f^o$ over this range. Estimated accuracy, ± 2 kJ.

(b) This is the low free energy of combustion of CO_2 and $H_2O(g)$ (analogous to the low heating value for the fuel, LHV) . The high free energy of combustion to $CO_2 + H_2O(l)$ is calculated by adding -9.7 + 0.026 T kJ per mol of water in the combustion products.

(c) The limiting value for paraffinic hydrocarbons, C_nH_{2n+2}, at high n.

(d) These are natural substances with varying properties; the values of ΔH_f^o and ΔH_c^o given here are for the Clifty Creek No.6 high-volatile bituminous coal whose molecular formula calculated from the ultimate analysis is $C_{0.54}H_{0.45}S_{0.01}N_{0.01}$

(e) For a wood of formula $C_{0.32}H_{0.46}O_{0.22}$, ΔG_c = 17.75 J/g in International Critical Table , Vol.11, P.131

2.2.3 Manufacture of Methanol

At present the most important method of methanol manufacture is a medium pressure process using hydrogen and carbon monoxide with a small amount of carbon dioxide . Carbon dioxide can react with hydrogen to form methanol as follows.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (2.4)$$

Fig. 2 .2 is a simplified flow diagram of high-pressure synthesis of methanol from carbon monoxide and hydrogen.

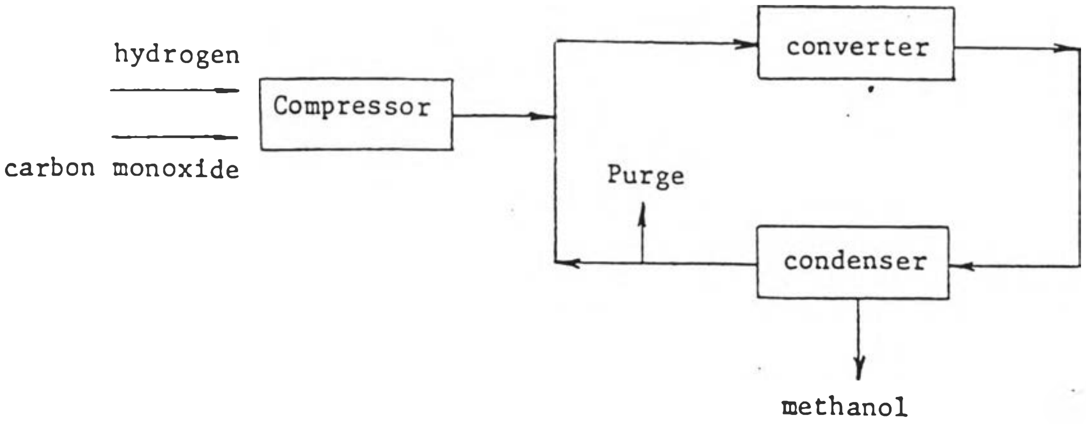


Fig.2.2 Flow sheet for methanol synthesis from carbon monoxide and hydrogen(J.M., 1968)

The following process details are limited to the carbon monoxide process. A gas mixture of CO and H_2 is adjusted with hydrogen gas until the approximate ratio of one volume carbon monodixe to two volumes of hydrogen is obtained.Mixed gases are compressed in multistage units to pressure of 3000 - 5000 psi, and partially preheated. Heated gases pass into a copper-lined steel converter, which contains a mixed catalyst of the oxides of zinc, chromium, manganese, or aluminium; for example, zinc oxide with 10%

chromium oxide. Reaction temperature is controlled at approximately 300°C by heat removal from the exothermic reaction and proper space velocity. The converter is heated initially to start the reaction, but the reaction is self-supporting once it is started.

The methanol containing gases leaving the reactor are cooled by the reactants in heat exchangers and condensed under full operating pressures. The pressure is released, and the cooled (0 to 20°C) liquid methanol is run off. It may be further purified by distillation. The residual gases are returned to the system for reprocessing. Accumulation of inert gases is guarded against by purging a part of the recycle gases. Methanol of 99% purity is obtained, using this process, and the equilibrium yeild is better than 60%.

Two main variables in the synthesis of methanol are the source of feed gas, and specific operating conditions. A number of the more important sources of reactants are given below : (W.F., 1957).

1. Coal and water may be reacted to form coke and then blue-water gas.

$$CO_2 + H_2O \longrightarrow 2CO + H_2 \qquad (2.5)$$

The water gas is purified and fortified with additional hydrogen obtained from coke-oven gas.

2. Natural gas is desulfurized by passage over activated carbon and subsequently preheated and mixed with carbon dioxide and steam at 30 psig and 800°C

$$3CH_4 + CO_2 + 2H_2O \longrightarrow 4CO + 8H_2 \qquad (2.6)$$

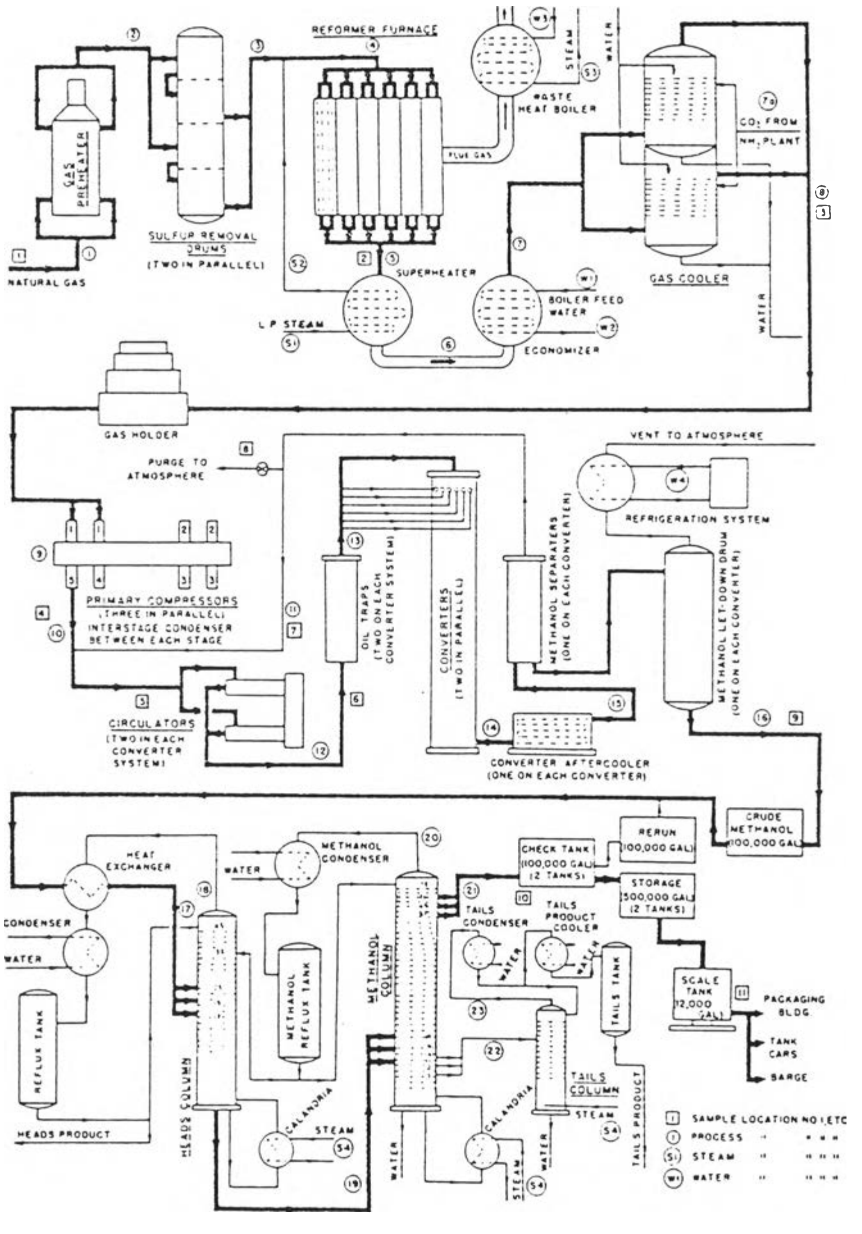


Figure 2.3. Flowsheet for methanol synthesis from carbon dioxide and hydrogen.

3. Partial oxidation of methane or other light hydrocarbons.

4. Fermentation by - product gases which contain hydrogen and carbon dioxide in about equal proporties.

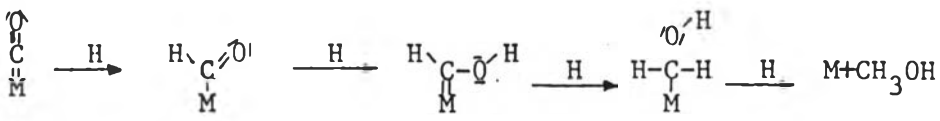
5. By - products gases, mostly carbon monoxide, from calcium carbide furnace.

6. Hydrogen obtained from electrolysis of water and brine.

2.2.4 Mechanism of Methanol Synthesis from CO and H_2

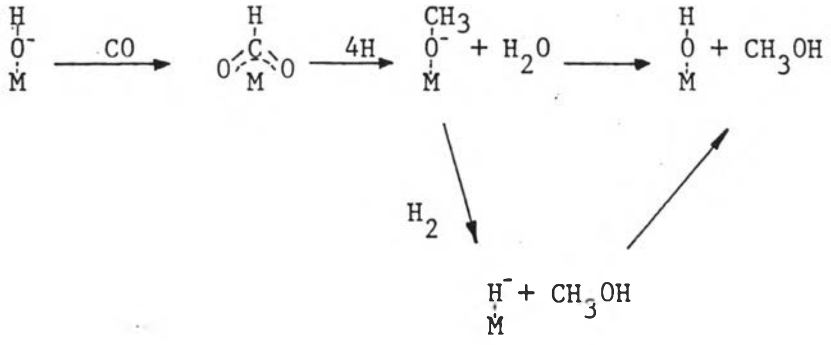
Mechanistic interpretation of the kinetic models may be as follows. Equilibria of carbon monoxide and molecular hydrogen between the gaseous phase and adsorbate are rapidly established. While the CO and H_2 molecules undergo dynamic exchange between the gas and adsorbed phase and among the surface sites, a small fraction of each, proportional to their surface concentrations, is activated for a reactive collision. The activation may involve splitting of hydrogen molecules into atoms, and partially hydrogenated species may include formyl HCO, formaldehyde HCHO, hydroxy-carbene HCOH, hydroxymethyl CH_2OH, and methoxyl CH_3O. With the participation of oxygen atoms of the solid oxide, of carbon dioxide, or water, formate $HCOO^-$ is also a possible intermediate. Once the reactive collision has occurred, the subsequent partial reactions are irreversible and rapid. For this reason, the kinetically significant intermediates are difficult to detect during the synthesis by either physical or chemical methods, and consequently the synthesis mechanism has not been firmly established. Yet it is very important to understand some fundamental features of the synthesis pathway because knowledge of mechanistic details will allow the control of selectivity to side products, where desirable, and pave the way for the design of catalysts for alkylations with the synthesis gas and other related reactions.

The mechanisms proposed in the past may be divided into three basic groups: carbon-down, represented by the sequence



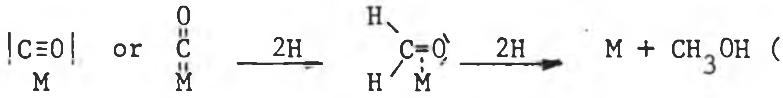
(I)

oxygen-down represented by the sequence



(II)

and side-on hydrogenation



(III)

Here M is a symbol for a site involved in the activation of carbon monoxide.

It is helpful to summarize briefly the thermodynamic energies of the various intermediates in pathways I-III. Figure 2.4 shows enthalpies and Gibbs free energies at 250°C which would be required for noncatalyzed reactions that involve a particular set of intermediates. Pathway II is drawn in Fig. 2.4 for potassium hydroxide, formate, methoxide, and hydride because of the lack of available thermodynamic data for the corresponding compounds of zinc and copper. Nevertheless, the relative values of ΔG and ΔH illustrate the points to be made. The role of the catalyst for Scheme I would be to lower the 200 kJ/mol thermodynamic barrier by suitable bonding of hydroxycarbene HCOH, while pathway II would require destabilization of the surface formate and methoxide. It is also seen that the removal of surface methoxide by hydrolysis would proceed with a lower thermodynamic barrier than by hydrogenation. Pathway III would seem to be a feasible one because the free energy of formaldehyde lies only 17 kJ/mol above that of methanol. However, formaldehyde has never been observed as intermediate in methanol synthesis over ZnO/Cr_2O_3 and Cu/ZnO catalysts. On the other hand, formaldehyde was frequently found to be the product of methanol decomposition. It is therefore likely that large kinetic barriers exist for the synthesis of formaldehyde that offset the thermodynamic feasibility of pathway III. It is evident that entirely different requirements would be imposed on catalysts for pathways I,II, or III: route I would require stabilization of hydroxycarbene, route II destabilization of formate and methoxide, and route III lowering of the kinetic barrier for formaldehyde synthesis. In the effort to detect some of the intermediates listed in Fig 2.4 various workers in the field resorted to experimental method, which gave partial insight into the methanol synthesis mechanisms.

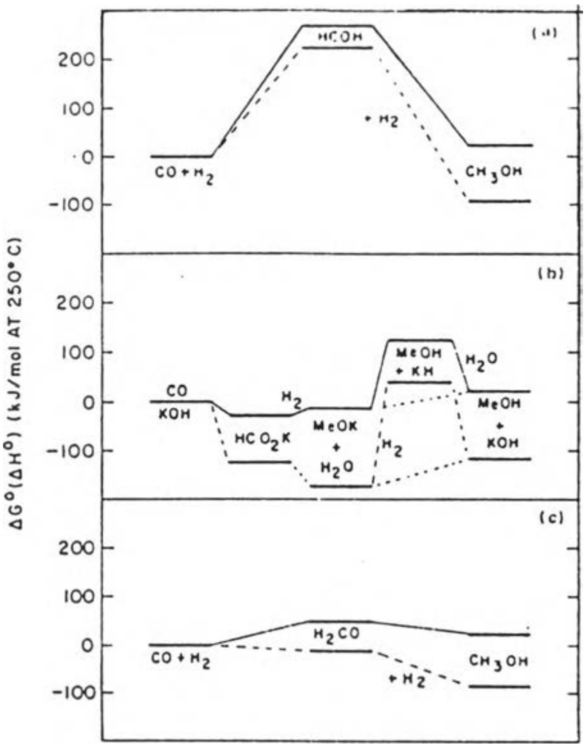


Fig. 2.4 Standard enthalpy (dashed lines) and Gibbs free-energy (full lines) changes for intermediates in methanol synthesis.

(a) Pathway I: hydroxycarbene route

$$CO(g) + H_2(g) \longrightarrow HCOH(g), \quad HCOH(g) + H_2(g) \longrightarrow CH_3OH(g)$$

(b) Pathway II: formate-methoxide route

$$CO(g) + KOH(s) \longrightarrow HCOOK(s)$$

$$HCOOK(s) + 2H(g) \longrightarrow CH_3OK(s) + H_2O(g)$$

$$CH_3OK(s) + H_2O(g) \longrightarrow CH_3OH(g) + KOH(s)$$

(c) Pathway III: formaldehyde route

$$CO(g) + H_2(g) \longrightarrow H_2CO(g), \quad H_2CO(g) + H_2(g) \longrightarrow CH_3OH(g)$$

2.2.5 Catalyst

Traditionally, methanol has been produced by catalytic hydrogenation of carbon monoxide. Several generations of catalysts have been developed. Zinc-chromium oxide was one of earliest used (see section 2.1 literature survey). Later, a catalyst based on a mixed zinc-copper oxide supported on chromium oxide or aluminium oxide was introduced. Tables 2.3,2.4 summarized the catalysts and the conditions used in the current processes (K.K., 1982).

There are recent reports that matallic catalysts of Pt,Pd, Ir, and Rh as well as homogeneous catalysts of $Rh(CO)_5$ and $HCO(CO)_4$ are also selective methanol synthesis catalysts.

Catalyst Selection

Methanol synthesis from carbon monoxide formally consists of an attachment of three hydrogen atoms onto the carbon end and of one hydrogen atom onto the oxygen end of the CO molecule without the cleavage of the carbon-oxygen bond. The two bonding Π orbitals of carbon monoxide, the lone pair (5σ) orbital or carbon, and the σ orbitals of two hydrogen molecules are utilized to make three C-H sigma bonds, one O-H sigma bond,and one additional lone pair orbital on the oxygen atom. schematically.

$$\begin{array}{c}\mathrm{H}\ \ \mathrm{H{-}H}\\ |\,|\mathrm{C{\equiv}O}|\\ \mathrm{H}\end{array} \longrightarrow \begin{array}{c}\mathrm{H}\\ \mathrm{H{-}C{-}\overline{\underline{O}}{-}H}\\ \mathrm{H}\end{array}$$

The carbon-oxygen sigma (3σ) and the lone-pair oxygen (4σ) orbitals remain intact except for a change in electron repulsion.

These features of the reaction impose the following requirements on the catalyst :

1. The catalyst must not cleave the carbon-oxygen sigma bond (~360 kJ/mol).

2. The catalyst must activate carbon monoxide molecule so that hydrogenation can occur on both ends of the molecule.

3. The catalyst must be a fairly good hydrogenation catalyst which activates hydrogen molecules in a manner suitable for the reaction. From the pattern of bonds broken and formed. This appears to require splitting of hydrogen molecules on the catalyst surface at some stage of the reaction.

Although all three requirements must be satisfied by a good methanol catalyst, there is evidence that activation of carbon monoxide is more difficult than that of hydrogen. It is therefore instructive first to examine the ability of various catalysts to activate CO by nondissociative chemisorption.

For metals there exists a clear-cut relationship between their position in the periodic table and their ability to chemisorb CO dissociatively. A division line has been established for ambient temperature by Broden et al. (K.K., 1982) between metals that chemisorb CO nondissociatively and those which have at least some crystal faces that split the CO molecule into surface carbon and oxygen. Table 2.5 shows a section of the periodic table wherein elements on the right-hand side of the borderline adsorb CO nondissociatively and vice versa. Broden et al. have also demonstrated on the basis of UV photoelectron spectroscopic measurements that the π-4σ energy separation is affected by the bonding of undissociated carbon monoxide to the metal surface: the (π-4σ) energy gap increases with increasing strength of the carbon-to-metal

Table 2.3 *Cu/Zn/Cr Oxide Catalysts Used in the Synthesis of Methanol*

Composition[a] (wt. %)	Reactants[b]	Temp. (°C)	Pressure (atm)	Space velocity (hr^{-1})	Yield (kg $liter^{-1}$ hr^{-1})	Company
11:70:19	3	250		4000		Power-Gas Corp
15:48:37	3	270	145	10,000	1.95[c]	Jap. Gas-Chem. Co.
31:38:5	3	230	50	10,000	0.755	BASF
	4	230	50	10,000	1.275	BASF
33:31:36	3	250	150	10,000	1.1	Academic
	3	300	150	10,000	2.2	Academic
40:10:50	1	260	100	10,000	0.48[c]	T. HFA
40:40:20	2	250	40	6000	0.26	ICI
	2	250	80	10,000	0.77	ICI
60:30:10	1	250	100	9800	2.28	Metall-Gesellschaft

[a] $CuO:ZnO:Cr_2O_3$.

[b] 1. $H_2 + CO + CO_2$; 2. $H_2 + CO + CO_2 + CH_4$; 3. $CO + H_2$; 4. $CO + H_2 + O_2$; N_2 is sometimes used as a diluent.

[c] Kilograms per kilogram per hour.

Table 2.4 *Cu/Zn/Al Oxide Catalysts Used in the Synthesis of Methanol*

Composition[a] (wt. %)	Reactants[b]	Temp. (°C)	Pressure (atm)	Space velocity (hr^{-1})	Yield (kg $liter^{-1}$ hr^{-1})	Company
12:62:25	2	230	200	10,000	3.290	BASF
	2	230	100	10,000	2.086	BASF
23:46:30	3	240		20,000	2.5	CCI
24:38:38	2	226	50	12,000	0.7	ICI
35:45:20	1	250				Academic
53:27:6	1	250	50			ICI
60:22:8	1	250	50	40,000	0.5	ICI
	2	226	100	9600	0.5	ICI
64:32:4	3	250	50	10,000	0.3	Academic
	3	300	50	10,000	0.9	Academic
66:17:17	1	275	70	200[d]	4.75	DuPont
[c]	1	250	50	10,000		Academic

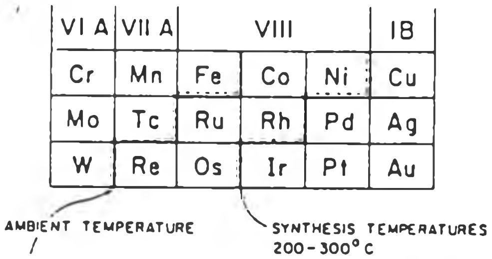
[a] $CuO:ZnO:Al_2O_3$.

[b] 1. $H_2 + CO + CO_2$; 2. $H_2 + CO + CO_2 + CH_4$; 3. $CO + H_2$; N_2 is sometimes used as a diluent.

[c] SNM-1 catalyst.

[d] Moles per hour.

Table 2.5 *CO Chemisorption on Transition Metals*[a]



VI A	VII A	VIII			IB
Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

---

[a] Dividing lines separate metals on the left which split CO from those on the right which adsorb CO nondissociatively.

[b] Brodén *et al.* (1976).

bond as is apparent from Table 2.6. The differences of the (π-4σ) energy gap for metals on the two sides of the room-temperature borderline are only tenths of electron volt (10 kJ) however, and it is entirely expectable that the borderline will depend on temperature. At high temperatures, cracking of carbon monoxide will become more probable, and so the borderline will move to the right. Although no measurements similar to those by Broden et.al. have been reported for elevated temperatures, the chemical behavior of various metal catalysts permits the conclusion that the division line between nondissociative and dissociative CO chemisorption lies, at 250-300°C, between nickel and copper, rhodium and palladium, and osmium and iridium. This high-temperature division line is also indicated in Table 2.5. At still higher temperatures, even copper and palladium will dissociate carbon monoxide.

It must be emphasized that nondissociative chemisorption of carbon monoxide, which appears to be a necessary condition for its hydrogenation to methanol, is not a sufficient prerequisite.

Table 2.6

Weakening of the C-O Bond by Back-Donation Metal $\longrightarrow$ CO($2\pi^*$)[a]

Mo,Fe	>	W	>	Ru	>	Ni	>	Pd	>	Ir	>	Pt
3.50		3.20		3.15		3.08		2.90		2.75		2.60

[a] Consequences: E(1π) increases more than E(4σ) and $\Delta(1\pi-4\sigma)$ increases with back-bonding. The average values of Δ for different transition metals are in electron volts. The scatter of Δ for different crystal faces is 0.2 eV (0.026 eV = 300 K).

For example,Ni and Ag chemisorb CO nondissociatively at ambient temperature but they are not methanol synthesis catalysts.Of the metals on the right-hand side of the high-temperature borderline in table 2.5 copper,palladium, platinum, and iridium have been reported to be selective methanol synthesis catalysts, while certain forms of rhodium have been found catalysts of intermediate activity and selectivity for methanol. All these metals have the common property that they lie close to the high-temperature borderline in Table 2.5. Moreover, metals guiding the synthesis selectively to methanol are to the right, but not far to the right, of this boundary. This indicates that good methanol catalysts chemisorb CO with moderate strength ,which is sufficient to perturb this melecule to enable it to react with hydrogen but insufficient to break it or any of the intermediates into fragments.

Aside from depending on the position of the metal in the periodic table as outlined above, the catalytic activity of each individual metal further depends on its physical and chemical state. Therefore, while the nondissociative chemisorption of CO serves as a crude guiding principle for the selection of a catalyst that will potentially snythesize methanol, the optimum performance of the catalyst results from maximizing and stabilizing its form that is most active, and in the case of methanol also most selective, under the desired reaction conditions.

Although most oxides adsorb CO associatively, the adsorption is weak and the CO molecule is not highly activated for the reaction. This difficulty can be partly circumvented by the use of a solid solution of oxides with the appropriate cations such that at least one of the cations binds CO strongly, as in Sn-Cu-O. An oxide with a high density of surface oxygen vacancies can also be desirable as the anion vacancies can assist in the adsorption and activation of CO by its interaction with the oxygen. Interestingly, an adsorbed CO with both the carbon and the oxygen ends interacting with the Ni surfaces may also be an important intermediate in the methanation reaction.

In addition to the ability to adsorb and activate CO, a good catalyst must also be able to activate hydrogen. However, this is usually not a limiting factor.

Finally, based on the assumed mechanism that the synthesis reaction proceeds via surface methoxide, an active and selective catalyst must not form a too stable metal methoxide. For the synthesis reaction to occur at a reasonable rate at 250°C, the activation energy for the rate-limiting step should not be higher than about 15 kcal/mole. Thus the heat of adsorption in the dissociative adsorption of methanol on a good catalyst should not be larger than 15 kcal/mole. In other words, this is the limit for the stability of the surface methoxide. In the decomposition of formic acid, the oxide catalysts can be classified as dehydrogenation catalysts or dehydration catalysts. (H.K.,1980)

By the principle of microscopic reversibility, one would expect that a good dehydrogenation catalyst in that reaction could also be a good methanol synthesis catalyst, as in the case of ZnO.

Factors that have contributed to the development of the low-pressure methanol catalyst have been the stability of metal dispersion; the choice of oxide "support"; the concentration of impurities such as alkali-, sulfur-, and chlorine-containing compounds; preparation variables giving rise to different precursor compounds; calcination and reduction regimes; etc.

After a complex preparation procedure, pinpointing the "active form" of a catalyst appears to be a difficult task. Experimental efforts to find the active component of a given catalyst often spur controversies, and the history of the copper-based methanol catalyst is a prime example of a collection of "puzzling results", claims and denials, and disagreements among the various workers in the field. After the successful development of the low-pressure process, debate has concentrated on the active component of the $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/Cr_2O_3$ catalysts. The palladium, platinum, iridium, and rhodium catalysts have not been considered for commerical applications because their activity was found to be significantly lower than that of the modern copper-based catalysts.

While the relation between the position of metal in the periodic table and their ability to synthesize methanol has been established, a similar pattern is lacking for oxides, such as basic oxides MgO, TiO_2 etc, and other main group oxides such as Al_2O_3 and SiO_2. It can be anticipated that the requirements 1-3 listed earlier, must also be satisfied by oxide catalysts but so far attempts have not been made to link the methanol synthesis activity of oxides with their physiochemical properties such as basicity or acidity, metal-oxygen bond strength, energy gap and semiconductivity, work function and electron affinity, etc. There does appear to be consensus among the workers in the field that surface acidity of oxide leads to the formation of dimethyl ether by a reaction consecutive to methanol synthesis.

Thus the above requirements could serve at best as very crude guidelines for a good catalyst. Furthermore, bulk properties alone are insufficient in characterizing a catalyst; detailed surface properties are needed.

2.2.6 Thermodynamic Chemical Equilibria:

The equilibrium between carbon monoxide, hydrogen and methanol is highly dependent on the temperature and on the partial pressures of the gases. For the reaction

$$CO \pm 2H_2 \rightleftharpoons CH_3OH\ (g) \tag{2.7}$$

the equilibrium constant is

$$K_f = \frac{f_{CH_3OH}}{(f_{CO})(f_{H_2})^2} = e^{-\Delta G/RT} \tag{2.8}$$

when f_x is the fugacity of the gases and where the Gibbs Free Energy is

$$\Delta G^o = \Delta H^o - T\Delta S^o$$
$$\simeq -25,100 + 56.8T \quad \text{cal/mol} \qquad (2.9)$$

Using a cubic heat capacity equation, Woodward gives the general free energy equation.

$$\Delta G^o = -74,622 + 67.28T \ln T - 0.04682T^2 + 4.259 \times 10^{-6}T^3$$
$$+0.339 \times 10^{-9}T^4 - 202T \text{ J/mol} \qquad (2.10)$$

More recent data can be used for more accurate results (see Table 2.7). At standard conditions the pressures approximate the activities, and thus

$$K_f \simeq K = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} \cdot \frac{\gamma_{CH_3OH}}{\gamma_{CO}(\gamma_{H_2})^2} \qquad (2.11)$$

$$= \frac{X_{CH_3OH}}{X_{CO}(X_{H_2})^2} \cdot K_\gamma \cdot P^{-2} \qquad (2.12)$$

where $K_\gamma = \dfrac{\gamma_{CH_3OH}}{\gamma_{CO}(\gamma_{H_2})^2}$

Strelzoff reviewed the experimental determinations, and concluded that the values obtained by Cherednichenko were a good average, namely

$$\log K = 3971T^{-1} - 7.492 \log T + 1.77 \times 10^{-3}T - 3.11$$
$$\times 10^{-8}T^2 + 9.218 \qquad (2.13)$$

Values of the fugacity ratio K_γ for methanol are calculated by Ewell and reproduced by Strelzoff. The mole fraction of methanol can thus be described by :

$$X_{CH_3OH} = \frac{K(X_{CO})\ (X_{H_2})^2 P^2}{K_Y} \qquad (2.14)$$

K_Y increases with temperature but decreases with pressure and K decreases with temperature. Therefore the equilibrium of methanol X_{CH_3OH} increases with increasing pressure but decreases rapidly with increasing temperature. This is in accordance with the basic oberevations of Le Chatelier's rule (the reaction is highly exothermic and three mols of reacting gases result in one of product). Thus high presssure and low temperature would move the reaction toward completion. Tables and graphs of the equilibrium composition as a function of initial compositions, temperature and pressure are given below.

Table 2.7 Properties of Methanol(W.H.,1967)

Molecular weight : 32.042 g mol^{-1}

Synonyms : carbinol, colonial spirit. colombian spirit, methyl alcohol, wood naphtha, wood spirit; French-alcool methylique; Italian-alcool metilico, metanolo; German-Methylalkohol: Polish-metylowy alkohol.

Temperaure	Refractive	Density	Vapor Pressure	
(^{o}C)	Index	(g cm^{-3})	(k Pa)	(mm Hg)
-20	-	0.8287	-	-
-10	-	0.8194	-	-
0	1.3361	0.8100	-	-
10	1.33224	0.8007	-	-
15	1.33034	0.7960	9.8856	74.15
20	1.32840	0.79131	13.0120	97.60
25	1.32652	0.78664	16.9575	127.19
30	1.32457	0.78196	21.8832	209.88
40	1.3207	0.7726	36.4677	266.03
50	1.3169	0.7633	55.6106	417.11
60	-	0.7546	84.6032	634.58
70	-	0.7448	-	-
80	-	0.7347	-	-
90	-	0.7242	-	-
100	-	0.7132	-	-

Density ρ_{SL} = A - Bt - C/(E - t) (Francis Equation)

Temperature	Parameters of Francis Equation			
t(^{o}C)	A	B x 10^{3}	C	E
-20 to 50	0.84638	0.9321	423.28	11,641
64-110	0.86867	0.6111	17.267	283.08

Vapor pressure from 288.15^{o} to 337.65 ^{o}K ;

$$\ln(P/kPa) = 15.76129944 - 2.845920984 \times 10^{3}K/T - 3.743415457 \times 10^{5}K^{2}/T^{2} + 2.188669828 \times 10^{7}K^{3}/T^{3}$$

Accuracy : T ± 0.002 K, P ± 1 Pa

Boiling point : 337.664 ± 0.002 °K, 64.514 °C

Melting point, triple point : -97.56 ± 0.02 °C

Critical temperature : 239.43 °C , 512.58°K

Critical pressure : 8.069 kPa (79.9 atm)

Critical density ρ_c = 0.272 g cm^{-3}

Heat of fusion: H = 32.13 ± 0.05 kJ mol^{-1}

Heat of vaporization 264.70°C, 760 mm Hg: H = 34.48 ± 0.04 kJ mol^{-1}

Standard States at 25°C

	Liquid	Gas
Heat of combustion H^o_c, kJ mol^{-1} to H_2O(liq.)	-726.13 ± 0.4	-764.08 ± 0.4
Heat of combustion H^o_c, kJ mol^{-1} to H_2O(gas)	-638.11	-676.05
Heat of formation H^o_f, kJ mol^{-1}	-239.03 ± 0.4	-201.08 ± 0.4
Entropy S^o, JK^{-1} mol^{-1}	127.24 ± 0.2	239.70 ± 0.2
Gibbs energy of formation G^o_f, kJ mol^{-1}	-166.82 ± 0.4	-162.42 ± 0.4
Heat capacity C_p, JK^{-1} mol^{-1}	81.17 ± 0.1	43.89 ± 0.1
Heat of dissociation H^o_d, kJ mol^{-1}	128.51 ± 0.4	90.56 ± 0.4

Thermodynamic functions of ideal methanol gas at one atmosphere:

Temperature (K)	Entropy ($J\ K^{-1}mol^{-1}$)	Heat Capacity ($J\ K^{-1}mol^{-1}$)	Heat of Formation ($kJ\ mol^{-1}$)	Gibbs Energy of Formation ($kJ\ mol^{-1}$)
0	0	0	-190.21	-190.21
273.15	235.94	42.47	-200.16	-165.60
298.15	239.70	43.89	-201.08	-162.42
300	239.99	44.02	-201.17	-162.17
400	253.59	51.42	-204.72	-161.17
500	265.73	59.50	-207.90	-134.22
600	277.48	67.03	-210.58	-119.24
700	288.32	73.12	-212.80	-103.85
800	298.57	79.66	-214.60	-88.12
900	308.24	84.89	-216.10	-72.22
1,000	317.44	89.45	-217.19	-56.19

Conversion factor of 4.1840 J/cal assumed.

Table 2.8 Calculated Equilibrium Constant for the Reaction (Y.W., 1952)

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

Temperature °C	G^o cal/mol	K	Temperature °C	G^o cal/mol	K
0	-7147	527,450	350	12,400	4.458×10^{-6}
100	-1766	10.84	400	15,279	1.091×10^{-6}
200	3832	1.695×10^{-2}	450	18,148	3.265×10^{-6}
250	6671	1.629×10^{-3}	500	21,023	1.134×10^{-6}
300	9530	2.316×10^{-4}			

where $$K = \frac{X_{CH_3OH}}{X_{CO} \times X_{H_2}^2} \times \frac{\gamma_{CH_3OH}}{\gamma_{CO} \times \gamma_{H_2}^2} \times P^{-2}$$

where X = mole fraction at equilibrium, P = total pressure (atm), and γ = fugacity coefficient of the gas. The term $X_{CH_3OH}/X_{CO} \times X_{H_2}^2$ is referred to as K_N, $\gamma_{CH_3OH}/\gamma_{CO} \times \gamma_{H_2}^2$ as K_γ, so that $K = K_N \times K_\gamma \times P^{-2}$.

Figure 2.5 was a plot of log K against $\frac{1}{T}$. The calculations were based on the above equations. The results, however, are in fair agreement with experimental values.

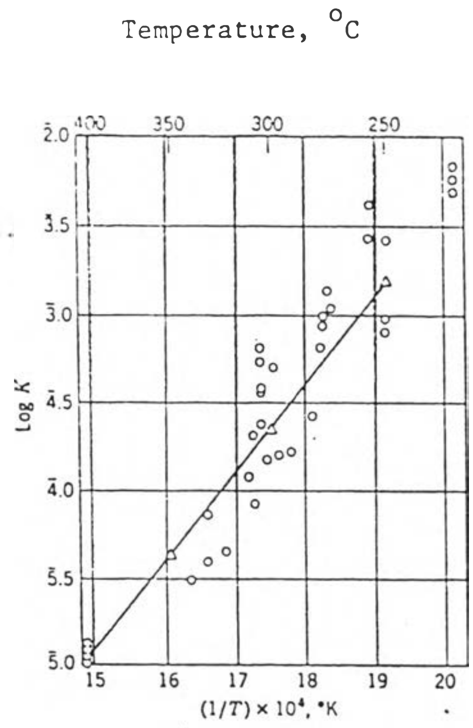


Figure 2.5 Equilibrium Constants of the Reaction $CO + 2H_2 \rightleftharpoons CH_3OH$. The encircled point refer to data obtained experimentally by different workers. The line represents calculated value (Y.W., 1952).

Figure 2.6 shows a set of isothermal curves of K_γ versus pressure for the reaction $CO + 2H_2 \rightleftharpoons CH_3OH$, calculated by Newton and Dodge . With the values of K_γ obtained from this graph, the effect of pressure on the reaction at 300°C was calculated See Table 2.9.

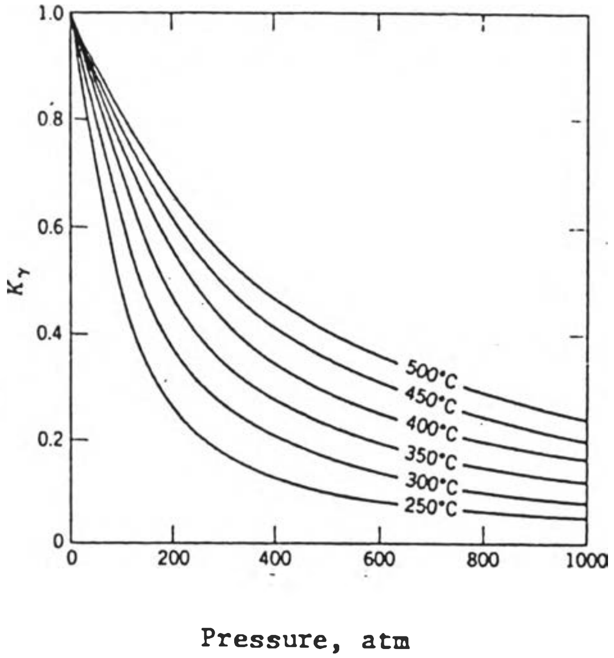


Figure 2.6 Values of K_γ for the Reaction $CO + 2H_2 \rightleftharpoons CH_3OH$

Table 2.9 Effect of Pressure on the Reaction $CO + 2H_2 \rightleftharpoons CH_3OH$ at 300^oC ($K = 2.32 \times 10^{-4}$)

Pressure,		Composition of equilibrium gases				Percent CO conversion to liquid CH_3OH in one pass
atm	K_γ	K_N	p_{CO} (atm)	p_{H_2} (atm)	p_{CH_3OH} (atm)	
10	0.96	0.0242	3.32	6.65	0.036	0.0
25	0.90	0.161	8.15	16.20	9.56	1.7
50	0.80	0.725	15.3	30.6	4.1	8.0
100	0.61	3.80	25.2	50.5	24.3	24.2
200	0.38	24.4	34.2	68.4	97.4	48.7
300	0.27	77.4	37.7	75.4	186.9	62.3

p_i = partial pressure of i-component

Although stoichiometry indicates a hydrogen-cabon monoxide ratio of 2:1, in industrial practice this is seldom used. Due to the difficulty in dispersing the heat of reaction, a ratio as high as 6:1 often is employed in the cycle gas; the excess hydrogen aids in dispersing the heat. This brings about an increased conversion of carbon monoxide to methanol although the conversion per pass on the basis of total gas charged will decrease. This illustrated in table 2.10.

Table 2.10 Methanol Conversion at Equilibrium at Different H_2-CO Ratios at 300 atm and 300°C

H_2/CO ratio	Percent CO converted to CH_3OH	Percent CH_3OH in exit gas
2:1	83.2	62.3
6:1	98.0	14.1

2.2.7 Kinetics

The rate at which conversion to the equilibrium concentrations is approached is however a much more complex function of the catalysts used and the conditions within the reactors. The overall reaction is a combination of the rates of reaction of the synthesis gas, less the rate of decomposition of the methanol. These in turn are modified by the catalyst and the composition and condition of the absorbed species. These are further complicated by nonideality of the gases. inhomogeneity in the chemical and physical characteristics of the catalyst, variations in temperature, and rates of the gases contacting the catalysts.

Natta et al (1953) developed the basic formula for the reaction rate for methanol synthesis which they based on the Langmuir absorption isotherm. This approach is probably the first thorough study of a heterogeneous catalytic reaction operated at high pressures; therefore, a detailed discussion of the method of treatment follows (N.G., 1954).

The following parts of the complex process have been considered separately :

(1) Diffusion of the gases from the bulk of the gaseous phases to the gas-catalyst interface.

(2) Chemisorption of each component gas at the active surface of the catalyst.

(3) Reactions among the chemisorbed gases, according to different kinetic hypotheses.

(4) Desorption of the reaction products.

(5) Diffusion of the reaction products from the gas-catalyst interface to the bulk of the gaseous phase.

Assumption was made, that the gaseous phase behaves as an ideal mixture of real gases, in which the following equality is valid:

$$a_i = x_i P \gamma_i$$

where

a_i = activity of the ith component in the gaseous phase.

P = total pressure of the system.

x_i = molar fraction of the ith component.

γ_i = fugacity coefficient of the ith component, calculated for the total pressure P and for the temperature of the experiment.

The processes (1) and (5) were so fast with the experimental values of space velocities and reactor shape, that their effect upon the kinetics of the reaction could be neglected. Therefore, with the assumption that the activity of each component at the interface catalyst-gas is equal to that of the component in the flowing gas phase, the adsorption rates of CO(A) and H_2(B) are :

$$r_A = K'_A a_A C_L - k''_A C_A$$

$$r_B = k'_B a_B C_L - k''_B C_B$$

where $r = \frac{dx}{dt}\frac{1}{W}$ is the resulting adsorption rate (the difference between adsorption and desorption rates expressed as the number of moles adsorbed by 1 gram of catalyst in unit time).

k' = adsorption rate constant

k'' = desorption rate constant

a = activity of the considered component at the interface catalyst-gas

C_L = molar concentration of the free active sites referred to the unit mass of the catalyst

C_A, C_B = concentrations of A and B, expressed moles of A or B adsorbed by the unit mass of catalyst

W = weight of the catalyst in grams

The following mechanism was assumed for adsorption on the active sites:

$$A + L \rightleftharpoons A^*$$

$$B + L \rightleftharpoons B^*$$

where L represents an active site. With the assumption that the reaction proceeds in the adsorbed phase, the following distinct schemes were considered:

(1) Bimolecular reaction

$$H_2^* + CO^* \rightleftharpoons H_2CO^* + L$$

$$r_{s_1} = \frac{S}{C_{L_0}} k'_{s_1} C_A C_B - \frac{S}{C_{L_0}} k''_{s_1} C_F C_L$$

$$H_2CO^* + H_2^* \rightleftharpoons CH_3OH^* + L$$

$$r_{s_2} = \frac{S}{C_{L_0}} k'_{s_2} C_F C_B - \frac{S}{C_{L_0}} k''_{s_2} C_R C_L$$

where S is the number of active sites located next to a given active site, and C_{L_0} is the molar concentration of active sites per unit of mass of the catalyst, and C_F and C_R the molar concentrations of formaldehyde and methanol, respectivity, adsorbed by unit mass of catalyst

(2) Trimolecular reaction

$$CO^* + 2H_2^* \rightleftharpoons CH_3OH^* + 2L$$

$$r_s = \frac{S^2}{2C_{L_0}^2} k'_s C_A C_B^2 - \frac{S^2}{2C_{L_0}^2} k''_s C_R C_L^2$$

where k'_s and k''_s are the rate constants for the direct and reverse reactions in the adsorbed phase.

For the desorption of methyl alcohol(R) the following mechanism, similar to the last one, was chosen:

$$R^* \rightleftharpoons R + L$$

$$r_A = k_R C_R - k'_R a_R C_L$$

From the experimental work of Natta and his co-workers (N.G.,1954) it has been concluded that the processes of adsorption and desorption proceed at much higher rates than the reaction at the surface, and that the process which determines the rate of the reaction is that of reaction among the adsorbed molecules. On that basis, it was possible to admit the existance of equilibrium between the activity of each component in the gas phase and its concentration in the adsorbed phase. If follows then:

$$C_A = K_A a_A C_L$$

$$C_B = K_B a_B C_L$$

$$C_R = K_R a_R C_L$$

where the constants K_A, K_B, K_R are the equilibrium constants for the adsorption of the components A, B, R.

The concentration of free active sites is given by the difference between the molar concentration of all sites C_{L_0}, and that of the filled sites :

$$C_L = C_{L_0} - (C_A + C_B + C_R + C_1)$$

where C_1 represents the concentration of the sites filled with other components which may be present (for example, inert substances). Operating in the absence of inert gases, it follows that

$$C_L = \frac{C_{L_0}}{1 + K_A a_A + K_B a_B + K_R a_R}$$

Substitution of the above value of C_L in the expressions which give the rate of reaction in the adsorbed phase, leads to expressions which give the reaction rate as a function of the rate constants of the direct and inverse reactions, of the constants of adsorption, and of the concentrations of active sites C_{L_0}.

These constants may be calculated on the basis of the kinetic data, whenever a sufficient number of accurate experimental data are available.

It has been shown that the kinetic equations, based on the hypothesis that the surface reaction is bimolecular, do not fit the isothermal rate curves.

Only with the hypothesis of a trimolecular reaction was it possible to solve this problem. The rate of a surface reaction for a trimolecular reaction results:

$$r = \frac{s^2 k_S' C_{L_0} K_A a_A K_B^2 a_B^2 - s^2 k_s'' C_{L_0} K_R a_R}{2(1 + K_A a_A + K_B a_B + K_R a_R)^3}$$

Considering that the ratio $\frac{k_s'}{k_s''}$ is equal to K^*, i.e., to the equilibrium constant of the reaction in the adsorbed phase, and that the thermodynamical equilibrium constant K_{eq} is related to the constants of equilibrium for the surface reaction by the relationship

$$\frac{K^* K_A K_B^2}{K_R} = K_{eq}$$

the following equation is easily obtained :

$$r = \frac{a_A a_B^2 - a_R / K_{eq}}{(A + Ba_A + Ca_B + Da_R)^3}$$

The four constants A, B, C, D represented in this equation are all positive and all of them are functions of the temperature only, if the assumption is made that the number of active sites C_{L_0} is independent of temperature. Substitution of the activities with the products of partial pressures and fugacity coefficients :

$$a_A = \gamma_A \rho_A; \quad a_B = \gamma_B \rho_B \quad \cdots\cdots$$

gives

$$r = \frac{\gamma_{CO}\rho_{CO}\gamma^2_{H_2}\rho^2_{H_2} - \frac{\gamma_{CH_3OH}\,\rho_{CH_3OH}}{K_{eq}}}{(A + B\gamma_{CO}\rho_{CO} + C\gamma_{H_2}\rho_{H_2} + D\gamma_{CH_3OH}\rho_{CH_3OH})^3} \qquad (2.15)$$

Equation (2.15) interprets the surface reaction according to the following scheme :

$$CO^* + 2H_2^* \rightleftharpoons CH_3OH^* + 2L$$

For a very short contact time, starting with methanol-free gases the concentration of methyl alcohol is nearly zero, and therefore Eq.(2.15) is thus simplified :

$$A + B\gamma_{CO}\rho_{CO} + C\gamma_{H_2}\rho_{H_2} = \sqrt[3]{\frac{\gamma_{CO}\rho_{CO}\gamma_{H_2}\rho_{H_2}}{r_o}} \qquad (2.16)$$

In Eq. (2.16) r_0 is the initial reaction rate, or, in other words, the tangent of the reaction isotherm at the origin.

Equation (2.16) contains three unknowns, whose correspondent constants may be determined by measuring the initial rates of reaction in three experiments performed at the same temperature, but at different pressures and composition. This was done at several different temperatures, and the values of A, B, C were determined as functions of temperature. To establish the values of the constant D, the values of A, B, C, as previously determined, were substituted in Eq. (2.15) which was solved by introducing the experimental r values resulting from different values of time factor and with the experimental values of the partial pressures of CO, H_2, CH_3OH.

2.2.8 Side Reactions.

Theoretically, carbon monoxide and hydrogen can react to form products other than methanol. A list of typical side reactions is given in Table 2.11

Table 2.11 Typical Side Reactions in Methanol Synthesis from Carbon Monoxide and Hydrogen.

Side reaction	ΔH^o_{25} (cal/mol)	ΔG^o_{25} (cal/mol)	ΔH^o_{327} (cal/mol)	ΔG^o_{327} (cal/mol)
(1) $CO+3H_2 \rightleftharpoons CH_4+H_2O$ (g)	-49,250	-33,970	-52,040	-17,270
(2) $2CO+5H_2 \rightleftharpoons C_2H_6+ 2H_2O$ (g)	-82,960	-51,520	-87,585	-17,580
(3) $3CO+7H_2 \rightleftharpoons C_3H_8+3H_2O$ (g)	-118,910	-71,095	-125,115	-20,830
(4) $CO+2H_2 \rightleftharpoons CH_3OH$ (g)	-21,684	- 5,900	-24,250	10,800
(5) $2CO+4H_2 \rightleftharpoons CH_3OCH_3$ (g)+H_2O (g)	-49,250	-16,320	-52,850	18,720
(6) $2CO+4H_2 \rightleftharpoons C_2H_5OH$ (g)+H_2O (g)	-61,190	-29,320	-64,610	4,520
(7) $3CO+6H_2 \rightleftharpoons C_3H_7OH$ (g)+$2H_2O$ (g)	-98,800	-53,000	-103,660	-4,400
(8) $2CO+2H_2 \rightleftharpoons CH_4+CO_2$	-59,110	-40,780	-61,360	-21,220
(9) $3CO+3H_2 \rightleftharpoons C_2H_5OH$ (g) + CO_2	-71,040	-36,140	-73,920	570
(10) $2CO \rightleftharpoons C(s)+CO_2$	-41,220	-28,640	-41,465	-15,730

It is seen that formation of paraffin hydrocarbons (reactions 1-3, 8) is favored thermodynamically over the methanol reaction at all temperatures, and that high pressures should have the greatest favorable effect on reactions (4-7) and (9). Some of the side reactions may represent a composite methanol synthesis-methanol decomposition, for example.

$$\begin{array}{llr} CO + 2H_2 & CH_3OH & (2.17) \\ CH_3OH + H_2 & CH_4 + H_2O & (2.18) \\ \hline CO + 3H_2 & CH_4 + H_2O & (2.19) \end{array}$$