5.3 OXYGENATE SYNTHESIS AND PROCESSES[3]

5.3.1 Methanol Synthesis

5.3.1.1 Introduction and Historic Notes

At an annual rate of approximately three billion kg, methanol is one of the top ten organic chemicals produced in the world. It is catalytically synthesized by the reactions

$$CO + 2H_2 \rightarrow CH_3OH, \quad \Delta H^o_{600K} = -100.46 \text{ kJ/mol and} \quad \Delta G^o_{600K} = +45.36 \text{ kJ/mol} \qquad [1]$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \quad \Delta H^o_{600K} = -61.59 \text{ kJ/mol and} \quad \Delta G^o_{600K} = +61.80 \text{ kJ/mol}. \qquad [2]$$

Simultaneously occurring with methanol synthesis is the water gas shift (WGS) reaction:

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H^o_{600K} = -38.7 \text{ kJ/mol and} \quad \Delta G^o_{600K} = -16.5 \text{ kJ/mol}. \qquad [3]$$

The synthesis gas (SG) from which methanol is produced can be obtained by steam reforming of natural gas or naphtha and by gasification of coal. Depending on the source, SG contains different ratios of $H_2/CO/CO_2/(H_2O)$ and impurities.

The current major uses of methanol are: as raw material for production of formaldehyde, as solvent, and as a basic chemical for organic syntheses. Pure methanol also is a proven high-octane (~130) fuel for internal combustion engines and is used in racing cars. Blends of methanol with cosolvent alcohols are used in variable amounts as

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[3] This section was written by Kamil Klier, Lehigh University.

octane-enhancing additives in gasoline, and methanol can also be converted to other fuel alcohols by processes reviewed in Section 5.3.2. There are known drawbacks of cosolvent-free-methanol/gasoline blends, the most significant being a limited miscibility and phase separation in the presence of water.

The first catalysts used for methanol synthesis were based on the oxides, salts, and metals patented by Patart in 1921 (30). The ZnO/Cr_2O_3 catalysts were commercialized by BASF in the 1920's (31). During the late 1920's systematic studies of binary Cu/ZnO catalysts were carried out by Frolich and coworkers (32), who examined the synthesis of methanol at 20.7 MPa and the decomposition of methanol at 0.10 MPa at temperatures >593°K (320°C) as the Cu/Zn ratio in the catalysts was varied. Methanol synthesis catalysts based on $Cu/ZnO/Al_2O_3$ operating at 15-25 MPa were employed on an industrial scale in Poland in 1952 (33). A new generation of low-pressure (<10 MPa) and low-temperature (220-270°C) $Cu/ZnO/Al_2O_3$ catalysts was introduced by ICI in the late 1960's (34-36). ICI developed a technology with $Cu/ZnO/Al_2O_3$ catalysts which were most active and stable in a synthesis gas containing both carbon monoxide and carbon dioxide, as well as hydrogen.

Other companies such as Lurgi, Topsoe, and BASF also practice low-pressure methanol synthesis using the $Cu/ZnO/M_2O_3$ (M = Cr, Al) catalysts. The basic difference between the ICI and Lurgi engineering is the use of a multi-quench (ICI) and multi-tubular (Lurgi) reactors.

The modern low-pressure methanol synthesis is very selective, >99.5 percent to methanol by reactions [1] - [2]. The high selectivity achieved has to be appreciated in view of the fact that methanol is thermodynamically the least probable product of the SG conversion; i.e., other compounds are formed with a more negative free energy change than methanol. A graphic example is given in Figure 5-3, which shows the standard Gibbs free energy change at 600°K (327°C) in kcal/mol of carbon

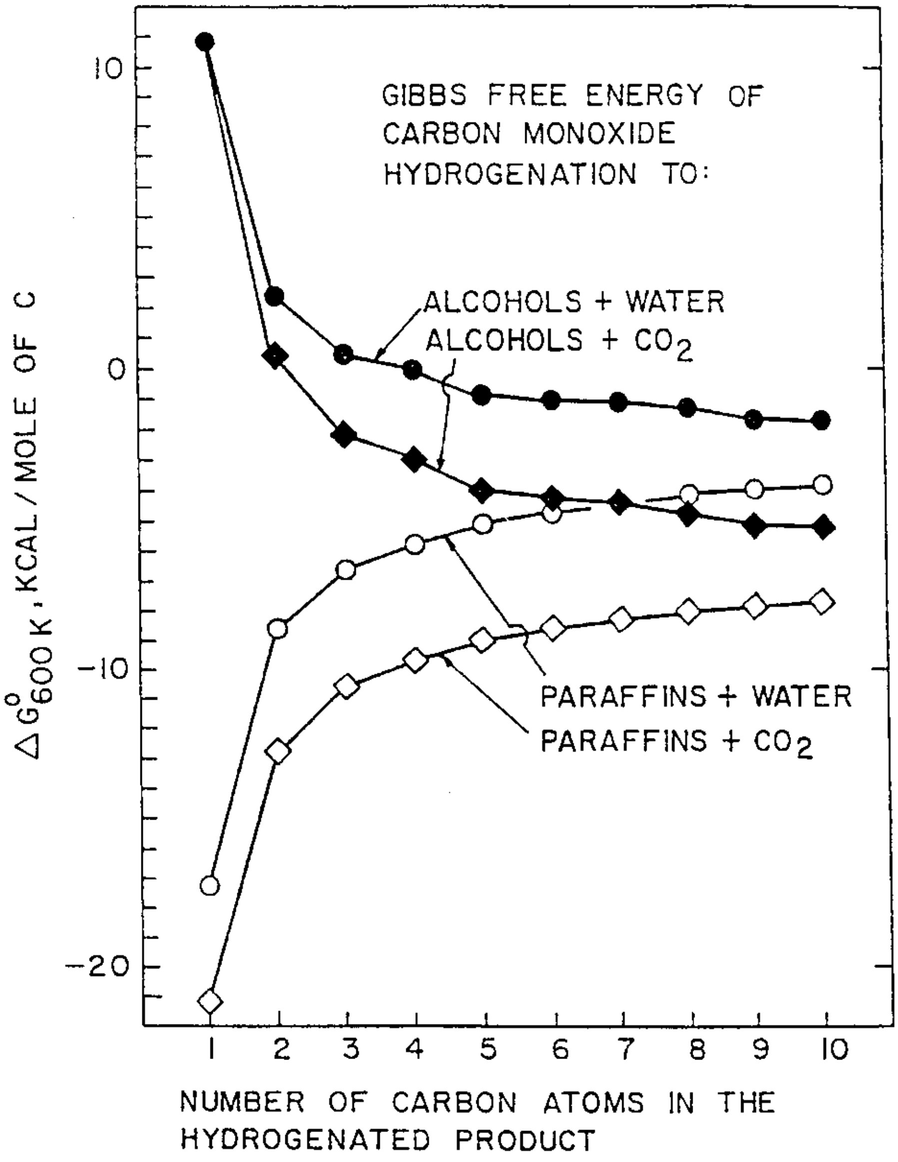


Figure 5-3. Gibbs Free Energy of Carbon Monoxide Hydrogenation

as a function of chain length n in the product C_n linear alcohols or paraffins generated by the reactions

$nCO + 2nH_2 \rightarrow CH_3(CH_2)_{n-1}OH + (n-1)H_2O$ (●) [4]
$(2n-1)CO + (n+1)H_2 \rightarrow CH_3(CH_2)_{n-1}OH + (n-1)CO_2$ (◆) [5]
$nCO + (2n+1)H_2 \rightarrow CH_3(CH_2)_{n-2}CH_3 + nH_2O$ (○) [6]
$2nCO + (n+1)H_2 \rightarrow CH_3(CH_2)_{n-2}CH_3 + nCO_2$ (◇) [7]

For long chains n, alcohols plus water formed by reaction [4] tend to have the same standard free energy as paraffins plus water by reaction [6], and alcohols plus CO_2 by reaction [5] the same standard free energy as paraffins plus CO_2 by reaction [7]. The difference for any single reaction type with water or CO_2 coproduct is given by the standard free energy of the water gas shift reaction [3], some -4 kcal/mol.

For short chains the free energies of formation for alcohols and hydrocarbons from CO/H_2 diverge, with hydrocarbons being significantly more favored. The greatest thermodynamic driving force is for the product methane (hydrocarbon with $n = 1$) plus CO_2 and the least thermodynamic driving force, in fact given by positive Gibbs free energy, is toward methanol (alcohol with $n = 1$). Because of the negative volume change of reactions [1] and [2], methanol synthesis can be thermodynamically driven against positive free energy by high pressures, but the catalyst must kinetically prevent the formation of all thermodynamically more favored products, i.e., hydrocarbons and C_2+ alcohols.

5.3.1.2 Existing Technology

Although methanol is a cheap commodity chemical ($0.72/gal in 1988), new plants (most for the low-pressure process) are being constructed all over the world. A staggering new or revamped annual capacity in excess of four billion kilograms of neat methanol has been completed, engineered, or planned in 1986-88, evidently with confidence in the future world market for fuel methanol (37). The ICI and Lurgi low-pressure technologies for methanol are described in some detail below.

The earlier high-pressure technologies are omitted in the present review because all new methanol plants built after 1967 have utilized the more modern low-pressure process. However, several high-pressure plants have been refurbished for higher-alcohol synthesis, and examples are given in Section 5.3.2.

A. The ICI Low-Pressure Process for Methanol

Although copper-based catalysts were known to be active and selective in methanol synthesis since the 1920's (38), they were not believed to be practical because of their low tolerance to sulfur poisoning and sintering of copper (39). Their practicality was proven when they were introduced in 1952 in a plant in Poland operating at 15-25 MPa (40) and in 1966 in an ICI (Imperial Chemical Industries) 109,500-tons-per-year plant at Billingham, U.K., that operated at pressures below 10 MPa. In 1972 ICI commissioned a 400,000-tons-per-year plant operating at 10 MPa and used a modified version of the original low-pressure methanol synthesis catalysts $Cu/ZnO/Al_2O_3$. The service life of the modern ICI catalysts is 3-4 years of continuous operation. The ICI technology spearheaded a worldwide commercially successful low-pressure (< 10 MPa) methanol technology that is responsible for the low prices of methanol in today's market. Two large ICI methanol plants are a part of the MTG (methanol-to-gasoline) complex at New Plymouth, New Zealand. In the mid-1980's over 75 percent of all new licensed methanol plants were based on the ICI process, accounting for one-third of the world's total methanol capacity. Plants ranging in size from 47,000 to 580,000 tons/year are in operation, and more are being built (37).

The ICI low-pressure methanol process is carried out at industrial sites that consist of a plant for producing the SG (H_2, CO, and CO_2 in various proportions), a low-pressure methanol synthesis plant, and a distillation plant. In most existing plants the source of SG is natural gas which is steam reformed to hydrogen-rich SG ($H_2/(2CO + 3CO_2) > 1$). Alternatively, the naphtha reforming process produces a nearly stoichiometric SG ($H_2/(2CO + 3CO_2) \approx 1$). Coal or heavy fuel oil, another source of SG, can be partially oxidized (gasified) to SG rich in carbon

($H_2/(2CO + 3CO_2) < 1$) that contains considerable quantities of sulfur. Because the copper-based catalysts are extremely sensitive to sulfur poisoning, the coal-derived SG must be purified to bring the sulfur content below 0.1 ppm. This can be achieved by several purification processes which operate by physical or chemical adsorption of acid gases, followed by a catalytic purification stage. The adjustment of hydrogen-to-carbon ratio suitable for methanol synthesis can be achieved by the water gas shift reaction between hydrogen-poor SG and steam. The flow diagram for the ICI low-pressure methanol synthesis from naphtha or natural gas is shown in Figure 5-4.

The synthesis loop contains a circulator, converter, heat exchanger, cooler, and separator. An ICI reactor of the quench gas converter type is shown in Figure 5-5. In this design there is a single catalyst bed with lozenge distributors for the injection of cold quench gas located at optimal depths of the catalyst bed. Good mixing of gases and temperature distribution in the reactor are ensured by this design. The distillation plant consists of a unit that removes volatile impurities such as dimethyl ether, esters, ketones, and iron carbonyl, and a unit which removes water and higher alcohols. After the first Billingham methanol plant was operated at 5 MPa since 1966, the pressure of 10 MPa was selected for the second, larger plant, with the carbon efficiency, defined as 100x(mols of methanol produced)/(mols of $CO + CO_2$ in the synthesis gas), 17 percent higher than that of the 5-MPa process. Pinto and Rogerson of ICI point out, however, that the above pressure advantage in efficiency holds only for hydrogen-rich SG from natural gas or naphtha and not for coal-derived carbon-rich SG (<u>40</u>).

The coal gasification conditions are usually such that SG with high CO/CO_2 ratio is obtained, which results in high carbon efficiencies over a wide range of pressures in the synthesis loop. Thus methanol synthesis is adaptable, without loss of carbon efficiency, to match a range of output pressures from various coal gasifiers. The general range of operating conditions of ICI low-pressure methanol plants is 5-10 MPa, 220-280°C, GHSV 5,000-60,000, and $H_2/(2CO + 3CO_2)$ ratios ≥ 1 but adaptable

Figure 5-4. ICI Low-Pressure Methanol Synthesis Process

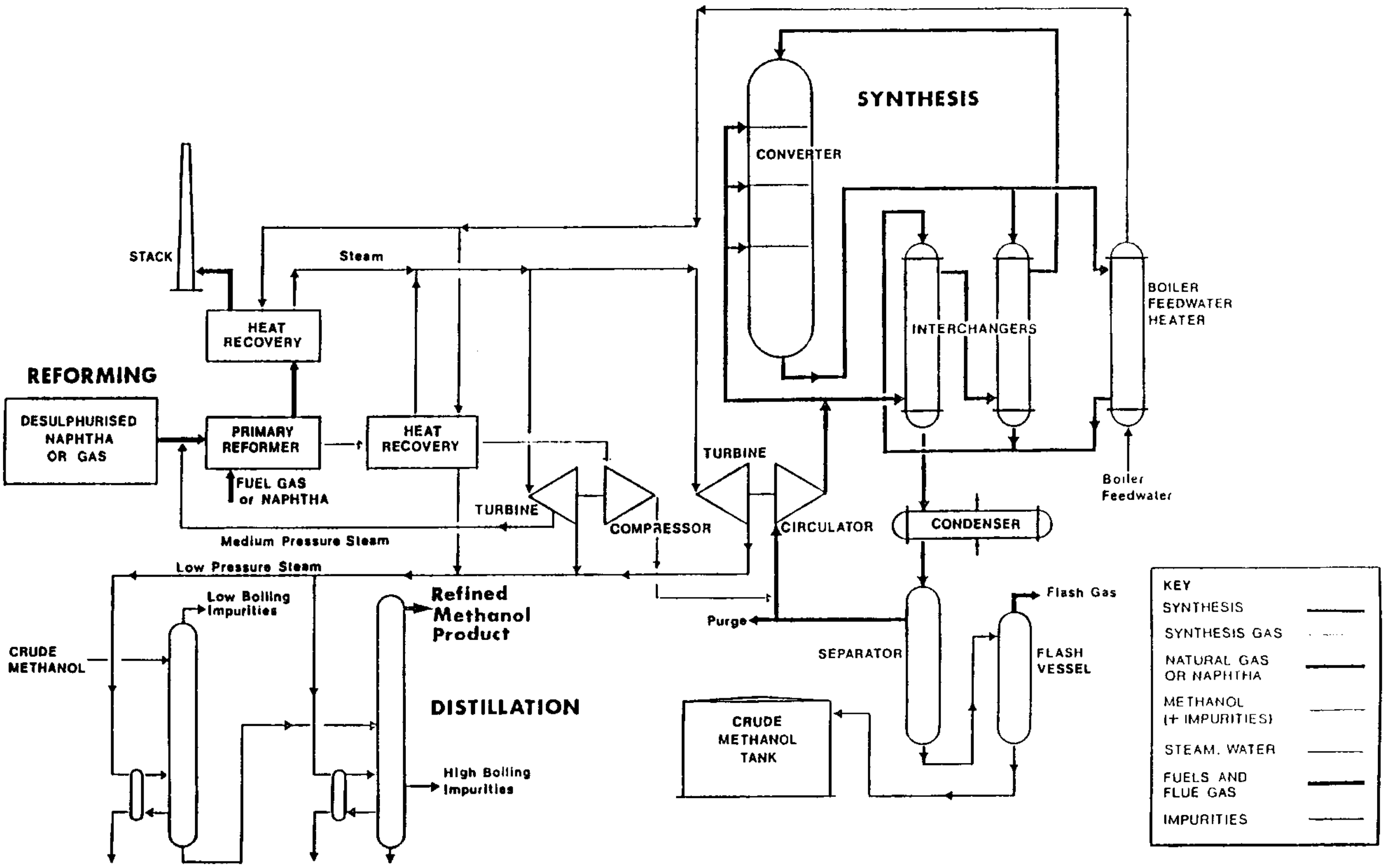
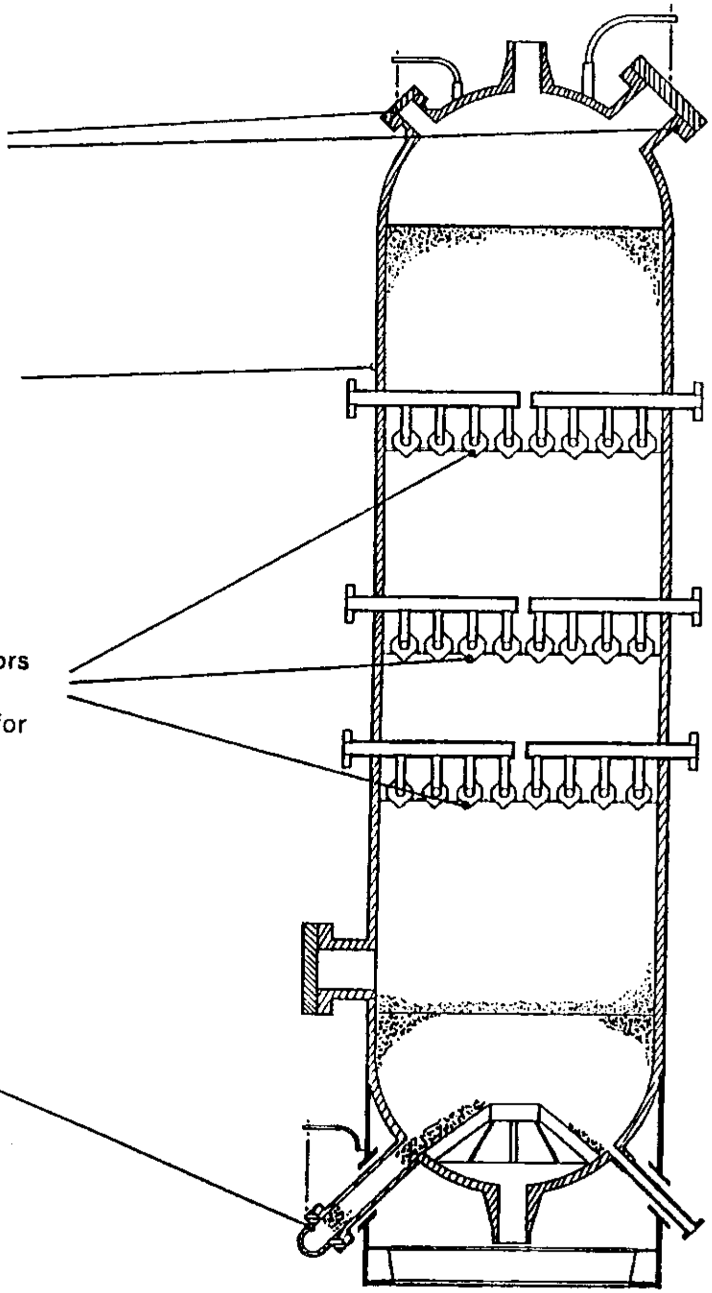


Figure 5-5. ICI Methanol Convertor



Catalyst can be readily charged and inspected through these manholes.

The pressure vessel is of a simple design readily manufactured in most parts of the world.

No internal catalyst basket is required.

The ICI Lozenge quench distributors ensure good gas distribution and allow the free passage of catalyst for charging and discharging.

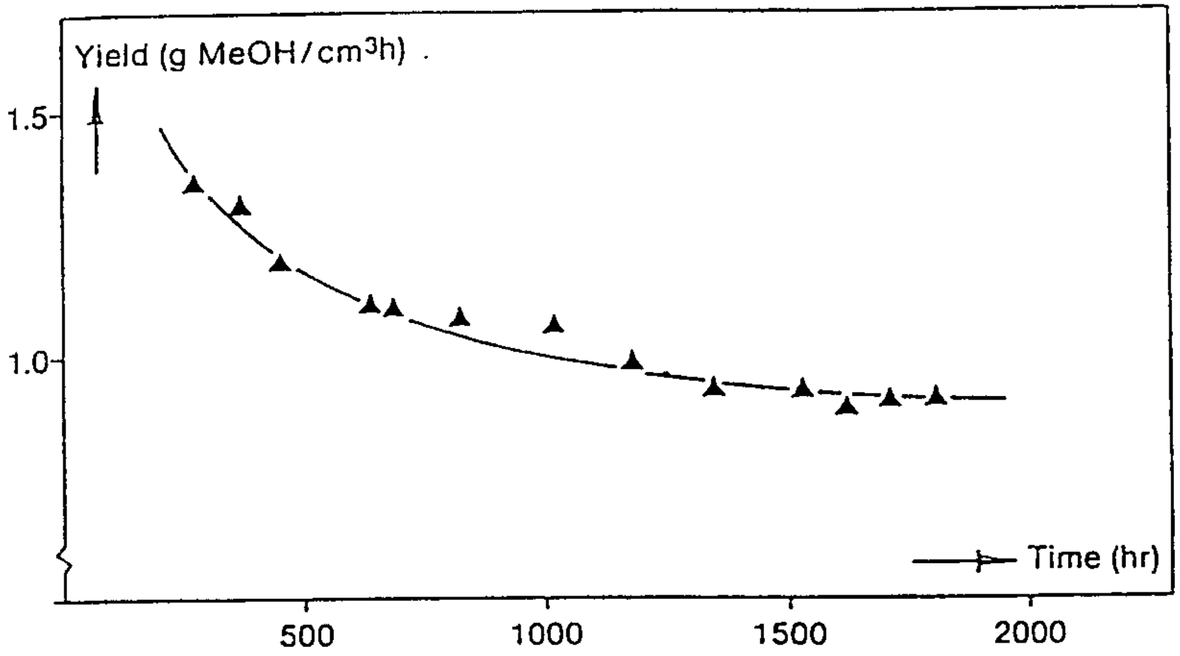
Gravity discharge of catalyst permits rapid preparation for maintenance or recharging.

to <1. Economic considerations have to take into account the energy and capital costs, and the main advantage associated with the use of coal-derived SG is that the SG compression can be avoided without penalty in carbon efficiency.

Although the ICI-type $Cu/ZnO/Al_2O_3$ catalysts have been optimized for maximum selectivity, STY's (space time yields), and long service life, they still deactivate, but no detailed reports on the rate of deactivation exist in the patent or open literature. In the recent review by Bart and Sneeden (41), an unpublished report of C. Boelens is quoted that presents deactivation data for an industrial $Cu/ZnO/Al_2O_3$ catalyst that operated for 2000 hours at 7 MPa and 240°C, as shown in Figure 5-6. In a 700-hour laboratory test of a binary Cu/ZnO catalyst at 7.5 MPa, 180-250°C, and variable SG ($H_2/CO/CO_2/H_2O$) compositions, Vedage et al. (42) detected no deactivation. In view of the results on deactivation of the copper-based catalysts under the more severe higher alcohol synthesis conditions described in Section 5.3.2.2, the main deactivation mechanism probably entails poisoning by chemical impurities, including trace iron carbonyl even in copper-lined reactors with pre-purified gases, rather than physical deactivation by redistribution of the elements in the catalyst and particle growth.

B. The Lurgi Low-pressure Process for Methanol

The Lurgi low-pressure technology also utilizes copper-based catalysts, principally of the composition $Cu/ZnO/Cr_2O_3$, the detailed preparation and additional promoter composition of which are not disclosed. The Lurgi reactor is a multi-tubular type, the tubes being filled with the catalyst and cooled with pressurized boiling water on the outside. The flow diagram of the Lurgi methanol synthesis from natural gas is shown in Figure 5-7. The natural gas is mixed with steam and converted to SG ($H_2/(2CO + 3CO_2)=1$) at 780°C and 4 MPa in the steam reformer 1 and autothermal reformer 2. High-pressure steam is produced in heat exchanger 3, and the SG is compressed to 7-10 MPa, preheated and fed into the reactor 4 together with the recycle gas. The reactor operates at 240-270°C, and good heat transfer to the pressurized boiling



Stability of industrial Cu/ZnO/Al_2O_3 catalyst. Reaction conditions: T 240 °C, p = 70 bar, S.V. = 35.000 h^{-1}

Figure 5-6. Stability of Industrial Cu/ZnO_3/Al_2O_3 Catalyst

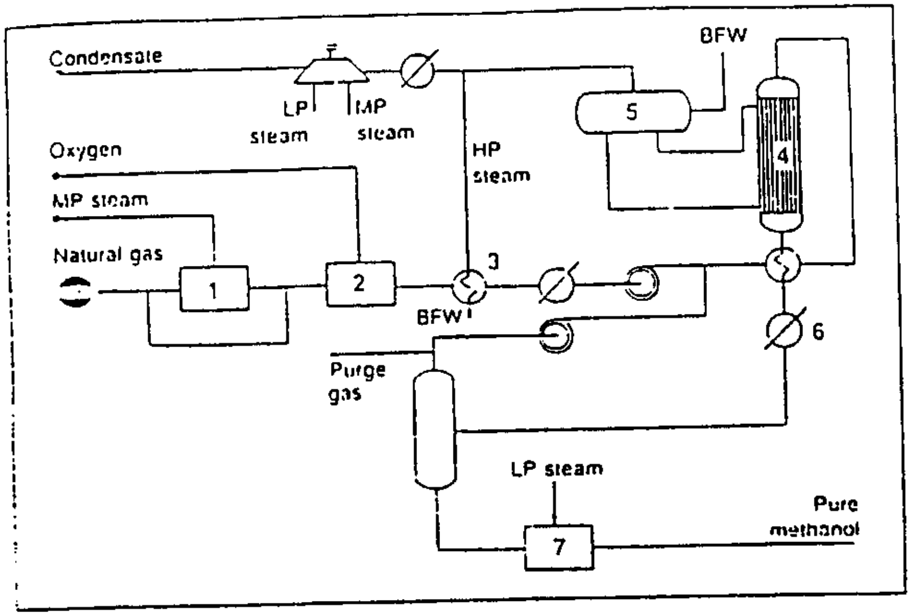


Figure 5-7. **Flow Diagram of Lurgi Methanol Synthesis**

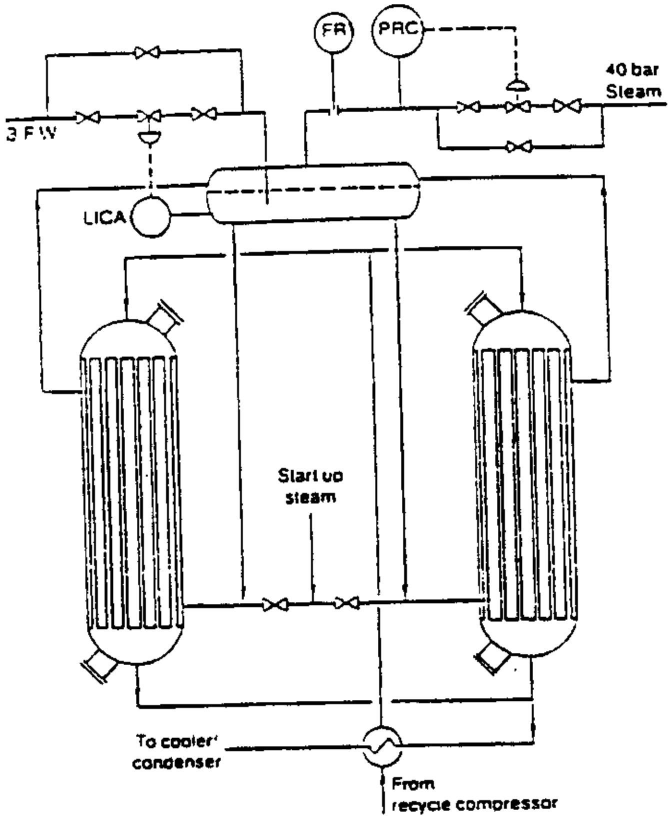


Figure 5-8. Lurgi Boiling-Water Low-Pressure Methanol Reactor

water that yields steam 5 is achieved. Methanol is produced at STY's close to 1 kg MeOH per liter of catalyst per hour. The crude methanol product is condensed 6, cooled, and distilled 7. The Lurgi tubular reactor is shown in greater detail in Figure 5-8.

The reactor has been called "quasi-isothermal" because of the smooth temperature profile along the reactor tubes, with exotherm variations not exceeding 10°C (43). The catalyst life is 3-4 years. The process can be easily adapted to utilize coal-derived SG by replacing the steam and auto-reformers by coal gasifiers and purification plant, mainly to remove sulfur from the SG. In early 1980 Lurgi Corporation was reported to have had almost 40 percent of the market for low-pressure methanol plants (43).

5.3.1.3 New Developments in Methanol Technology

Improvements in methanol technology have been sought by improved engineering and by novel catalyst design. Among the engineering developments are the Air Products and Chemicals (APCI)/Chem Systems liquid-phase methanol process and the gas-solid-solid trickle flow reactor (GSSTFR) developed at Twente University of Technology in the Netherlands and patented by Shell. Among the catalyst designs are some very active new heterogeneous copper-based catalysts that have been invented, but which are less selective and are poisoned by CO_2. Effort in the development of soluble "homogeneous" catalysts led to the two-stage Brookhaven process and to the soluble Cu(I)-sodium methoxide system of Union Carbide, with variable or not-yet-evaluated degree of success.

Another interesting development is the Shell process for direct synthesis of dimethyl ether (DME). Although DME-- CH_3OCH_3 -- contains two carbon atoms, it is often classified as a C_1 chemical because the two carbon atoms are not directly bonded with each other but rather connected via an oxygen bridge. Despite the claims, both in the patent (44) and open (45) literature, that alkali impurities are detrimental to the productivity and the selectivity of copper-based catalysts for methanol, Lehigh University discovered that heavy alkali promoters, particularly cesium, substantially enhance methanol yields from CO/H_2 while retaining 99 percent selectivity to methanol, when used in optimum concentrations.

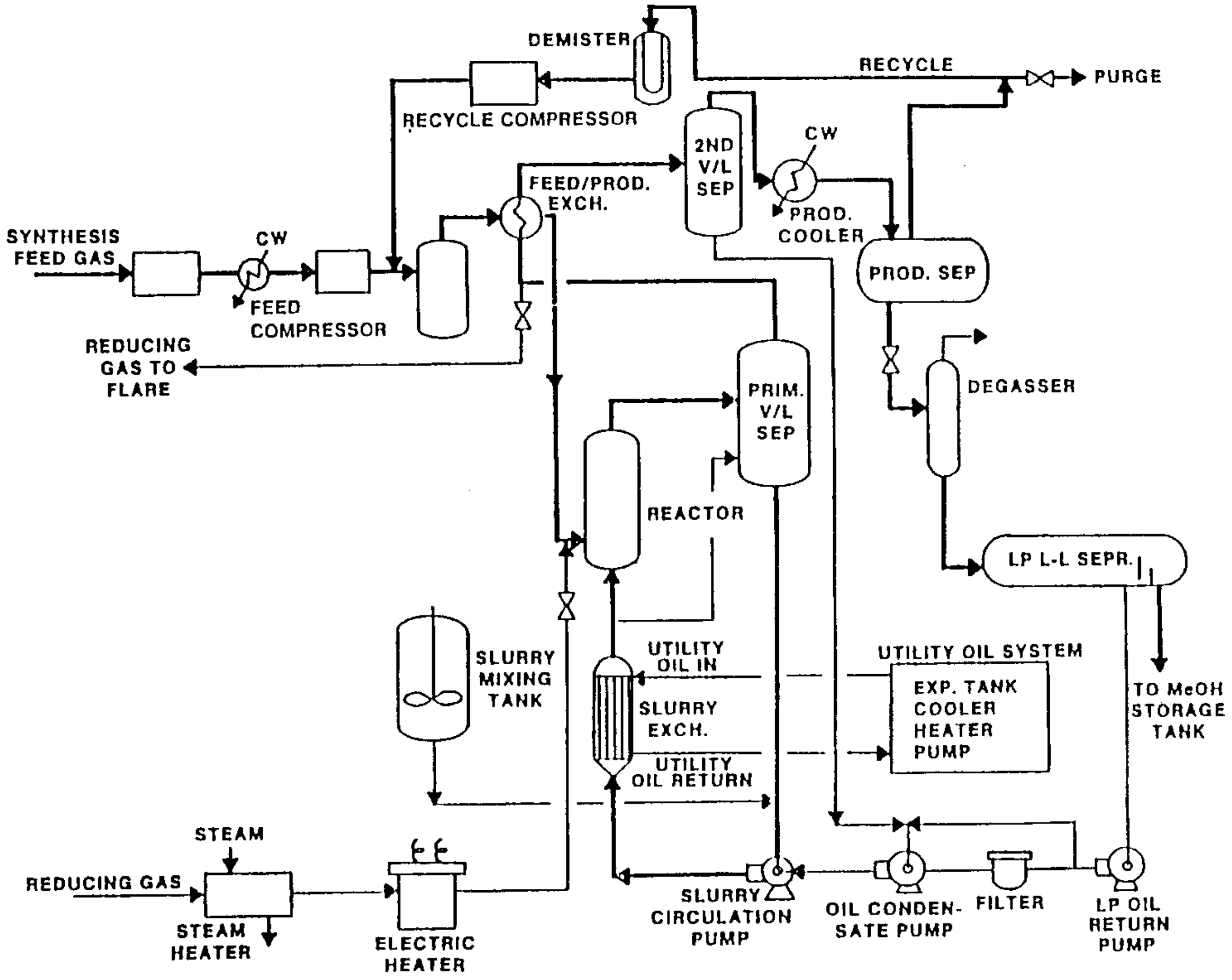
A. The APCI/Chem Systems Liquid-Phase Methanol Process

An engineering concept by which the reaction heat released in methanol synthesis is efficiently transferred to the surroundings utilizes a suspension of the heterogeneous catalyst in a liquid phase. In 1972 M.O. Tarhan of Bethlehem Steel was awarded a patent for methanol synthesis (actually by the reaction $3CO + 2H_2O \rightarrow 2CO_2 + CH_3OH$) utilizing Cu/ZnO catalysts suspended in water (46). In the mid-1970's Chem Systems developed a liquid-phase methanol synthesis in which a solid catalyst was fluidized or entrained in a hydrocarbon liquid, usually a mineral oil (47). The presence of the liquid renders the reactor virtually isothermal, and potentially higher conversions per pass could be achieved without catalyst deactivation in the hot spots of the reaction exotherm. Early research at Chem Systems utilized pelletized catalyst (3-6 mm particles) in an ebullated-bed reactor.

In 1981 DOE began supporting research on a liquid-phase methanol process in a Process Development Unit (PDU) at the LaPorte, Texas, plant operated by Air Products and Chemicals, Inc. (APCI). The Electric Power Research Institute (EPRI) cosponsored the program because of EPRI's interest in the economically attractive coproduction of methanol and electricity in integrated gasification-combined cycles (IGCC) (48). The LaPorte PDU was commissioned in March 1984. Five major synthesis runs and numerous hydrodynamic and analytical runs have been carried out. The flow diagram of the LaPorte PDU is shown in Figure 5-9.

The process operates at 3.5-6.3 MPa, 220-270°C, liquid-fluidized space velocity (l/kg cat/hour) 1000-4000, liquid-entrained catalyst loading 10-33 weight percent, and $H_2/CO/CO_2/(N_2$ + inerts) compositions 35/51/13/1 (CO-rich SG) and 55/19/5/19 (balanced SG). The CO-rich gas is representative of SG from modern coal gasifiers. These gases are suitable for once-through methanol synthesis in an IGCC process. The

Figure 5-9. Simplified Process Flow Sheet for LaPorte PDU



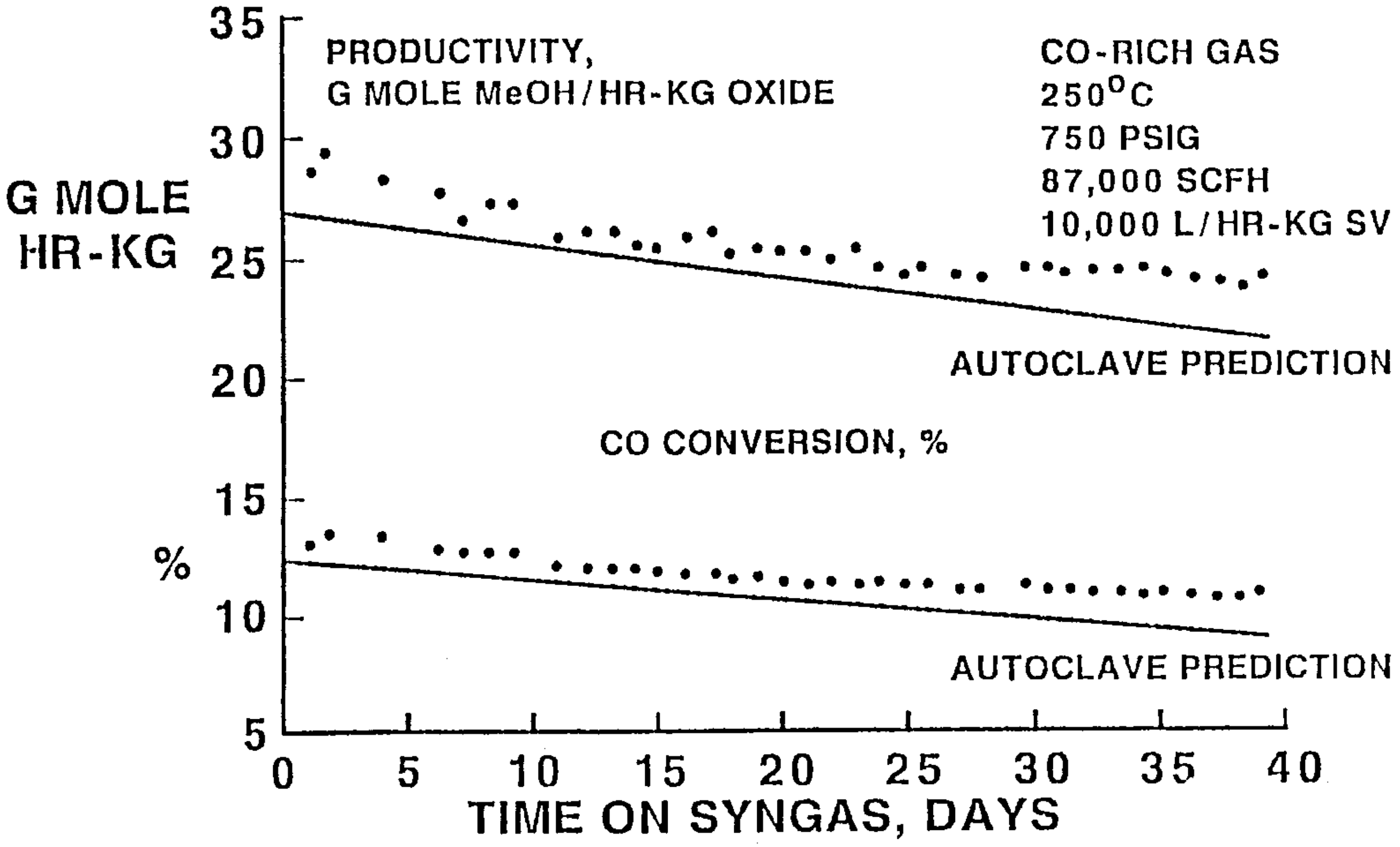
catalyst used was of $Cu/ZnO/Al_2O_3$ composition, and its powder slurry was circulated through the liquid-phase reactor.

The performance of the LaPorte process utilizing purified gases and metallurgical improvements aiming at minimizing catalyst deactivation by iron and nickel carbonyls is shown in Figure 5-10. Here it should be noted that the productivity expressed in Figure 5-10 in mol MeOH per kg catalyst per hour converts to STY in kg MeOH per hour per 1 of the liquid slurry in the reactor by a factor 0.032 (for the molecular weight of methanol in kg) x 0.25 (for 25 weight percent catalyst in slurry) = 0.008, giving an initial STY of 0.232 and an STY after 40 days (~1000 hours) of 0.19. The STY of the run reported in Figure 5-10 is less than 25 percent of the commercial ICI or Lurgi vapor phase processes, but a deactivation rate of 2.2 percent per 100 hours compares favorably with that for the vapor-phase process in Figure 5-6. It appears that the main factor reducing the STY in the liquid-phase process is the dilution of the catalyst by the liquid phase, and further development with a higher slurry density is underway (47).

B. The Gas-Solid-Solid Trickle Flow Reactor (GSSTFR)

In 1986 Hydrocarbon Processing reported an interesting engineering approach to shifting the equilibrium of reactions [1] and [2] in favor of the methanol product by adsorbing the synthesized methanol directly in the catalytic reactor (49) and removing it by a flow of the solid sorbent down the catalytic bed. The synthesis is conducted in a column reactor filled with a stationary bed of 5x5 mm cylindrical pellets of the catalyst (commercial BASF copper catalyst Type S3-85 was used in the Twente development work (49)) mixed with 7x7x1 mm Raschig rings. The SG is introduced at the bottom, and the selective adsorbent powder (amorphous LA-25 low-alumina AKZO cracking catalyst with mean particle diameter 90 μm) is introduced at the top and trickles downward over the catalyst pellets. The LA-25 sorbent adsorbs methanol at the reaction temperatures of 220-250°C, is collected in a bottom vessel, and is presumably ready for separation of methanol and recirculation of the sorbent.

Figure 5-10. LaPorte PDU 40-Day Run Performance, May/June 1985



Westerterp and Luczynski (49) estimated that the STY's of methanol are increased by 40 percent and 25 percent and more steam is produced in their type of GSSTFR compared to conventional reactors. The basic assumption was that the increased efficiency is due to shifting the equilibrium of reaction [1] or, in the presence of CO_2, of reaction [2]. Complete conversion of SG is achievable despite the unfavorable chemical equilibrium. The Twente University project has been sponsored by the Royal Dutch Shell Group since 1982, and Shell owns the patent (49).

C. New Catalytic Systems for Methanol Synthesis

This paragraph summarizes some new reports on heterogeneous and homogeneous catalysts for methanol synthesis, deferring the discussion of systems that make methanol with significant portions of higher oxygenates to Section 5.3.2. Moreover, one approach to the direct synthesis of dimethyl ether is discussed here.

Copper-Based Catalysts

Copper-based catalysts that are mixed, often on a nanometer scale, with the oxides of Zn, Al, Cr, Sc, V, Ti, Si, Mg, Th, and lanthanides, have been investigated in many recent studies. Some of these studies are summarized in Table 5-2. Most of these investigations are aimed at resolving mechanistic questions and effects of supports, dopants, and different preparation modes.

No higher activities or selectivities than those of the industrial $Cu/ZnO/Al_2O_3$ (58) or model binary Cu/ZnO (59) catalysts were reported, but the following established properties of copper-based catalysts were confirmed.

- o The $Cu/ZnO/Al_2O_3$ and Cu/ZnO catalysts can produce methanol with near - 100 percent selectivity.
- o The STY's of copper-based catalysts for methanol under the low pressure (< 10 MPa) conditions are the highest of all selective catalysts known today.

Table 5-2. **Activities and Selectivities to Oxygenates (Methanol and C_2+ Alcohols) of Catalysts Based on Copper**

Sources: 9th ICC, July 1988 and References 58-62.

General Conditions: 1-5 MPa, $H_2/CO/CO_2$ = variable, given in footnote, GHSV 4,000-10,000.

Catalyst	Selectivity to oxygenates percent	T °C	STY^{a} of oxygenates g/kg(l)cat/hour	Ref.
$Cu/ZnO/Al_2O_3/Cr_2O_3$	~100^{b}	230	12.0^{c}	50
$Cu/ZnO/Al_2O_3/Sc_2O_3$	~100^{b}	230	11.6^{c}	50
$Cu/ZnO/Al_2O_3/V_2O_3$	~100^{b}	230	7.4^{c}	50
$Cu/ZnO/Al_2O_3$	~100^{b}	230	5.0^{c}	50
Cu/ZnO	99	250	796.0^{d}	51
Cu/TiO_2	0.5	250	2.1^{e}	51
$Cu/ZnO/Al_2O_3$	~100^{b}	250	800.0^{f}	52
$Cu/ZnO/Al_2O_3$	~100^{b}	215	1216.0^{g}	53
$Cu/ZnO/ZrO_2$ aerogel	96	300	432.0^{h}	54
Cu/ZrO_2^{j}	n.a.	160-300^{k}	453.0^{i,k}	55
$Cu/Co/ZrO_2$	64	250	28^{l}.0	56
$Cu/Co/TiO_2$	25	250	27.0^{l}	56
$Cu/Co/SiO_2$	66	250	9.0	56
Cu/Co/MgO	85	250	19^{l}.0	56
$Cu/Co/Al_2O_3$^{m}	-	-	-	57
$Cu/ZnO/Al_2O_3$	>99	230	1430.0^{n}	58
Cu/ZnO	>99.8	250	1350.0p	59
$CuI/NaOCH_3$	n.a.	110	85.0^{q}	60
Cu/CeO_2	80-98	240	816.0^{r}	61
Cu/La_2O_3	n.a.	240	384.0r	61
Cu/ThO_2	n.a.	250	960.0^{s}	62

[a] STY = Space Time Yield, given in g of oxygenated product per kg of catalyst (including support) where available, otherwise per liter of catalyst.

[b] Only methanol reported, pressure not given.

[c] $H_2/CO/CO_2$ = 66/28/6, GHSV 6000.

[d] Pressure 1.7 MPa.

[e] This catalyst is very active in methanol decomposition, however.

[f] Pressure 5 MPa, $H_2/CO/CO_2$ = 70/25/5.

Table 5-2 (continued)

g Pressure 5 MPa, $H_2/CO/CO_2$ = 65.5/30.9/3.6.

h Pressure 3.2 MPa, $H_2/CO/CO_2$ = 9/0/91.

i Pressure 5 MPa, $H_2/CO/CO_2$ = 80/0/20.

j Urea-precipitated catalyst.

k Precise reaction temperature at which the tabulated STY was obtained is not given.

l Pressure 1 MPa, $H_2/CO/CO_2$ = 67/33/0.

m Study of preparation only; hydrotalcite precursors give rise to homogeneous Cu-Co-Al mixed oxide spinel-type structure which upon reduction yields small crystallites of Cu and Co metals and $CoAl_2O_4$ spinel.

n Pressure 5 MPa, $H_2/CO/CO_2$, GHSV 10,000.

p Pressure 7.5 MPa, $H_2/CO/CO_2$ = 70/24/6, GHSV 5000 per kg of catalyst.

q Pressure 13.5 MPa, $H_2/CO/CO_2$ = 50/50/0, STY estimated from a batch autoclave experiment, methanol and methyl formate (1:1:8).

r Pressure 5 MPa, $H_2/CO/CO_2$ = 50/50/0, GHSV 72,000 per liter of catalyst = 180,000 - 240,000 per kg of catalyst.

s Pressure 6 MPa, $H_2/CO/CO_2$ = 70/30/0, GHSV 22,000.

- CO_2 can be hydrogenated to methanol as efficiently as or faster than CO, but the highest rates are obtained with $H_2/CO/CO_2$ feed in which CO/CO_2 ratios = 10/1 - 4/1 are used.
- Addition of a Group VIII metal such as Co lowers the selectivity to methanol and increases the selectivity to C_2+ alcohols but also increases the hydrocarbon make.

A relatively novel support for methanol copper catalysts is ZrO_2, an amphoteric solid that imparts stability on the catalyst while preserving high selectivity and yields of methanol. On the other hand, TiO_2 drastically lowers both the selectivity to and the yields of oxygenates and promotes hydrocarbon formation.

The question of the nature of active forms of copper (Cu^+ vs. Cu°) was re-investigated in several papers, and a number of reports were published, some inconclusive (51, 55), some favoring Cu^+ (50, 53, 54) and another favoring Cu° (52). Obviously, while much evidence in favor of electron-deficient copper has been gathered (58), the nature of the catalytically active valence state of copper deserves further attention. The question is an important one because if Cu^+ is the active state, then catalysts can be designed so that Cu^+ is maximized. This was attempted by Tsai et al. (50) through doping the $Cu/ZnO/Al_2O_3$ catalyst with a trivalent element M^{3+} of ion size compatible with the ZnO lattice such as Cr^{3+}, Sc^{3+}, and V^{3+}. These trivalent ions dispersed in ZnO stabilize Cu^+ by valence induction, $2\ Zn^{2+}{}_{Zn} = Cu^{+}{}_{Zn}M^{3+}{}_{Zn}$. Tsai et al. obtained evidence by Auger spectroscopy that the valence induction doping procedure was particularly successful with Cr^{3+} and Sc^{3+}, and more active catalysts relative to his reference $Cu/ZnO/Al_2O_3$ were obtained. Unfortunately, the reaction pressure in Tsai's et al. work was not given, and the STY's over all their catalysts appeared low for the normal range of pressures used, which is around 5 MPa.

Researchers at the U.S. Bureau of Mines at Reno discovered that Cu/ThO_2 catalysts prepared from intermetallic $CuTh_x$ alloys by a redox process were active in methanol synthesis (62). Following this discovery, ICI researchers probed into a larger class of intermetallic

$CuMe_x$ (Me = Ce, La, Pr, Nd, Gd, Dy, Zr, Ti, and Th) alloys as precursors of Cu/Me_2O_3 and Cu/MeO_2 catalysts, and found that the $CuCe_{0.5}$, $CuLa_{0.45}$, and $CuPr_{0.5}$ precursors also resulted in very highly active catalysts for the synthesis of methanol from CO/H_2 (61). These catalysts were severely poisoned by small amounts (1-2 percent) of CO_2 and often contained copper metal of low dispersion (very large particles, Cu metal area $< 1\ m^2/g$). An electropositive copper species analogous to that proposed by Klier et al. for the Cu/ZnO catalyst (59), Baglin et al. for the Cu/ThO_2 catalyst (62), and Shibata et al. for the Cu/ZrO_2 catalyst (63) was tentatively suggested to be the active component. Alternative candidates for the site for methanol synthesis were suggested to be extremely small copper particles (<1 nm diameter) or intermetallic hydrides.

Because of the lack of tolerance to CO_2, the Cu intermetallics-derived catalysts, although very highly active, were not considered practical as industrial SG invariably contains amounts of CO_2, and CO_2 removal (to below 0.1 percent) may adversely influence process economics. The oxygenate selectivities of these catalysts of 80-98 percent are acceptable in their upper limit but not in the lower limit. After initially higher activities, steady states were attained in 20-40 hours, and these are reported in Table 5-2, Rows 19 and 20. The concentration of CO_2 in the exit gas was typically less than 0.1 percent and that of H_2O approximately 1 percent of condensable products, or <0.05 percent by volume of the exit gas. The effect of water on the activity of the $CuMe_x$ intermetallics-derived catalysts has not been studied. Taking into account the very high activities, the lack of precise oxygen balances, the lack of precise determination of CO_2 effects at concentrations <1 percent, and the lack of data on water effects on the synthesis, it appears that these novel copper-based catalysts derived from intermetallics have not yet been studied in full detail and further research into their improvement is to be expected.

The Brookhaven Process for Methanol Synthesis

A 1984 report by Brookhaven scientists on a novel approach to methanol synthesis (64) received considerable attention. In this approach two catalyst components are used in the liquid phase, a metal (molybdenum) carbonyl that activates carbon monoxide and a hydride that hydrogenates the carbonyl to methanol and is regenerated by a reaction with hydrogen. In 1986 a further process development was reported by O'Hare et al. (65) wherein synthesis temperatures of 100°C were used, indicating extraordinary activities of the methanol synthesis. A. G. Mills points out (66) that there have been reservations about the practical operation of the Brookhaven process, for example, in terms of deactivation of the catalyst by CO_2 in the SG. Also, specific technical information has not been made public, and therefore the Brookhaven process yields and selectivities have not been verified. In the older version the selectivity ratio of methanol to methane that has been reported for temperatures around 200°C and pressures 2-5 MPa was between 45/55 and 55/45 (65). On the other hand, every new catalytic system that displays activity for methanol synthesis at temperatures below 200°C merits attention for possible future improvements of selectivity and stability, and further development of the Brookhaven system is to be expected.

Union Carbide's Soluble Cu(I) Catalysts for Methanol Synthesis

Union Carbide carried out research into soluble homogeneous catalysts for methanol under DOE contracts and published a final technical report in January 1987 (60). Ruthenium, cobalt, copper, and other catalysts were investigated. The ruthenium system, when promoted with iodine and lanthanide salts, yielded oxygenates with up to 80 percent of C_2+ alcohols, but the STY's of 60-100 g/l/hour were thought to require improvement to achieve commercially attractive yields. Although good stability of the halide-promoted ruthenium catalysts for direct conversion of syngas to alcohols was obtained, solvent degradation was found to be a problem with a number of solvents investigated. The homogeneous cobalt catalysts also produced alcohols but invariably at low rates, often with large amounts of methane side product; they also catalyzed solvent decomposition. Other catalysts based on soluble complexes of Fe, Re, Pd and Rh were found to produce very small or no amounts of alcohols.

Among the copper-containing catalysts studied, a very active copper-alkali system was investigated that produced significant amounts of methanol (30 g/l/hour) and methyl formate (55 g/l/hour) at temperatures as low as 110°C. The Union Carbide research aimed at the testing and improvement of a Japanese invention (66) that claimed a soluble copper catalyst for the production of methanol (MeOH) and methyl formate (MeOF) at moderate pressures (3-13 MPa) and very low temperatures (80-120°C) when sodium methoxide ($NaOCH_3$) was used as a promoter. Some of the results with the copper-sodium methoxide catalysts are summarized in Table 5-3. The data in run 86 in this table correspond to STY's of 85 g (MeOH + MeOF) per liter of the solution per hour at 110°C and show that the copper-sodium methoxide system is indeed active as well as selective, in the sense that it produces only MeOH + MeOF. However, mechanistically MeOF is a precursor of methanol in this system (cf. Section 5.3.1.4), and it is probably this mechanistic feature that gives rise to higher yields of MeOF than of methanol in this system. The copper-sodium methoxide catalyst has been found unstable and rapidly deactivated by precipitation of metallic copper from the solution of cuprous halide or hydride exposed to the synthesis gas $H_2/CO = 1/1$.

Although a selective homogeneous catalyst for methanol that could be considered as a replacement for the existing low-pressure heterogeneous catalysts such as the $Cu/ZnO/Cr_2O_3$ and $Cu/ZnO/Al_2O_3$ has not yet been found, several initially very active homogeneous catalysts have been reported as demonstrated above. There are incentives to continue a search for active and selective homogeneous methanol synthesis catalysts. Among the advantages of successful homogeneous catalysts are the following often-listed items (68):

- Liquid-phase systems in general have excellent heat-removal capability, and the added advantage that no cumbersome slurry handling or engineering is necessary with homogeneous soluble catalysts -- it can be expected that a good homogeneous

Table 5-3. Reactivity of Copper Hydride Systems (Soluble Copper Catalyst)

	SGHAM-G-#	RUN 86
1.	Catalyst	CuH
2.	mmoles	5
3.	NaOMe, mmol	110
4.	Solvent[a]	DEC
5.	mL	75
6.	Additive[b]	none
7.	mmol	0
8.	Press, psi	2000
9.	H_2/CO	1:1
10.	Temp., °C	110
11.	Time, hr	3
12.	Uptake, psi	4480
13.	Wt. % MeOH	7.0
14.	Wt. % MeOF	12.6
15.	Other Prods	none

[a] DEC = Diethyl carbitol

[b] NaOEt = sodium ethoxide

[c] Products included ethanol and ethyl formate derived from ethoxide.

catalyst in the APCI/Chem Systems liquid-phase process (Section 5.3.1.3) would be an attractive replacement for the slurried commercial catalyst that has been designed for vapor-phase processes.

- Homogeneous catalysts often allow improved selectivities under mild conditions -- this is not really the case in methanol synthesis, which is already 99.5 percent selective over heterogeneous catalysts, but can be the case in the related higher-alcohol synthesis.
- The absence of surface effects can lead to higher specific activity since the homogeneous catalyst is molecularly dispersed, and all catalyst molecules participate in the chemical reaction, as opposed to heterogeneous catalysts where supports and subsurface atoms do not.
- The claim of longer catalyst life has yet to be substantiated for heterogeneous methanol catalysts, the heterogeneous counterpart of which is usable for 3-4 years.
- The manufacture of homogeneous catalysts is simple and reproducible.
- A further advantage of homogeneous catalysts is that reaction kinetics in solutions are usually simpler than on the surfaces of heterogeneous catalysts, and the intermediates are somewhat more easily characterizable.

<u>The Shell Process for Direct Synthesis of Dimethyl Ether (DME)</u>

In 1983 L. H. Slaugh of Shell Oil Co. was awarded a patent for direct synthesis of DME from SG (<u>69</u>). Although DME -- CH_3OCH_3-- contains two carbon atoms, it is often classified as a C_1 chemical because the carbon atoms are connected by an oxygen bridge rather than being joined by a C-C bond. The Shell catalyst consists of the Cu/ZnO components for methanol synthesis supported on a 150-500 m^2/g gamma alumina. It can be assumed that two consecutive reactions occur on the catalyst, the methanol synthesis [1] and methanol dehydration to DME [8],

$$2CH_3OH \rightarrow \underset{\text{DME}}{CH_3OCH_3} + H_2O \qquad [8]$$

the reaction [1] occurring on the Cu/ZnO component and reaction [8] on the gamma-alumina component. Reaction [8] is usually acid-catalyzed, and it is expected that the gamma alumina imparts the acidic function onto the catalyst. Sodium impurities must be avoided as they could neutralize the surface acidity. Reaction [8] represents a sink for methanol, and the overall process [9] can be run with a minimum concentration of the methanol intermediate.

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O \qquad [9]$$

Selectivities up to 97 percent to DME, with 1.5 percent MeOH and 1.5 percent hydrocarbons coproduced, were achieved with the Shell catalyst at 6 MPa, 292-300°C, GHSV 3000, and the STY of DME exceeded 0.8 kg/l cat/hour, i.e., rates comparable to those of methanol synthesis at 250°C were achieved.

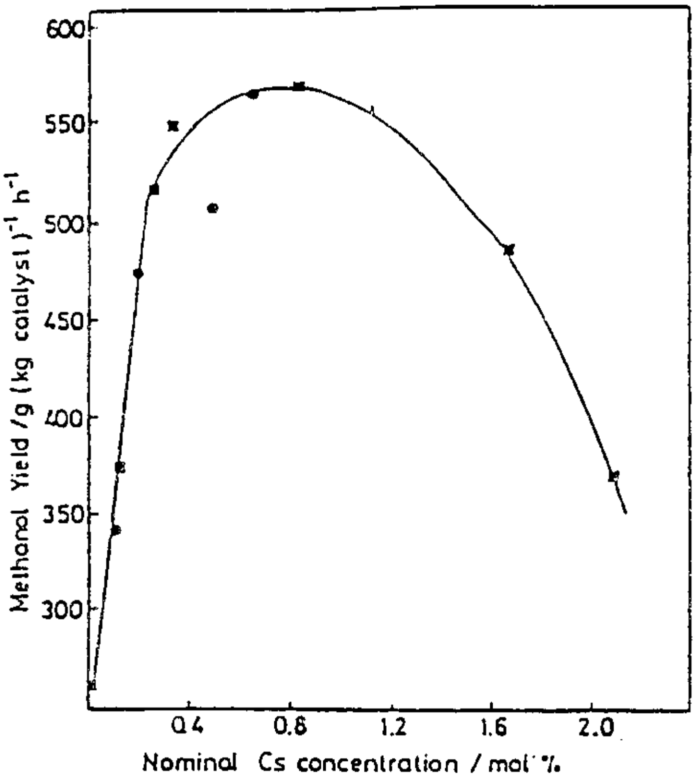
The Shell process for DME from SG utilizing modified low-pressure methanol synthesis catalysts is an example of a method of how SG can be converted to value-added chemicals via methanol as an intermediate. In conjunction with indirect liquefaction, the process for direct synthesis of DME may have an application in utilizing DME as a source for aromatic gasoline produced by the Mobil process utilizing the ZSM-5 zeolite. This concept would constitute a modification of the three-stage MTG process in which methanol is synthesized from SG and converted in a separate reactor over an acid catalyst to DME, with the DME being fed to the ZSM-5 to produce aromatic gasoline; the first two stages are integrated via Reaction [9] in the Shell DME process.

Enhancement of Methanol Yields over Cu/ZnO Catalysts by Alkali Dopants

After initial work that established the ion-specific promotion effects of Cu/ZnO catalysts by alkali hydroxides, Cs > Rb > K > Na,Li, for methanol and higher-alcohol synthesis (70), Lehigh University researchers have demonstrated that the alkali-promoted Cu/ZnO catalysts are quite selective for methanol under the usual methanol synthesis conditions, e.g., 7.6 MPa, 250°C, GHSV 6000, and $H_2/(2CO + 3CO_2) = 1.15$, and the methanol synthesis rates are at the same time enhanced. Further, it was found that several types of the dopant alkali compounds may be used, e.g., formates instead of hydroxides. The alkali dopants must used in their optimum concentration, as exemplified by the effect of cesium in Figure 5-11. It is seen from the data in this figure that the rate of methanol synthesis from H_2/CO was enhanced by a factor of 2.15 in the presence of the optimum Cs concentration of 0.3-0.8 percent and an STY of 0.56 kg MeOH/kg cat/hour at 7.6 MPa, 250°C, GHSV 6000 and $H_2/CO = 2.33$ was attained. With the use of higher-surface-area $Cu/ZnO/Cr_2O_3$ catalysts, 3 percent Cs doping increased the STY from 0.56 to 1.05 kg MeOH/kg cat/hour at the same conditions (except GHSV = 10,000) (72). For the Cs/Cu/ZnO catalyst the selectivity to MeOH was 99 percent and for the $Cs/Cu/ZnO/Cr_2O_3$ catalyst 98 percent, the main side products being methyl formate (0.6 percent for the Cs/Cu/Zn/Cr catalyst) and ethanol (1.3 percent for the Cs/Cu/Zn/Cr catalyst). Thus, STY's from a CO_2-free H_2/CO SG were achieved by Cs doping of the copper-based catalysts that are characteristic of the performance of copper-based methanol synthesis catalysts only in the presence of CO_2.

The activity of the Cs/Cu/ZnO catalysts was also investigated with a feed gas containing water ($H_2/CO/H_2O$ = 2.3/1/0-0.4), and it was found that the alkali dopant promoted the methanol synthesis rates also in the presence of large amounts of injected water. The kinetic behavior is complex and is shown in Figure 5-12. Although most of the injected water is converted to CO_2 by the water gas shift reaction [3], the direct effect of CO_2 in the feed gas on the STY of methanol has not been reported by the Lehigh group.

Associated with the Cs promotion of methanol synthesis exemplified in Figure 5-12 is the promotion by Cs of the water gas shift activity of the Cu/ZnO catalysts. The effects are large, up to by a factor of 2.3 (73), and it is evident that a very highly active WGS catalyst has been discovered in the studies of alkali-doped copper-based methanol synthesis catalysts. The long-term stability of the $Cs/Cu/ZnO/(Cr_2O_3)$ catalysts has been studied under the higher-alcohol synthesis conditions (Section 5.3.2.2), and a deactivation rate of 1.6 percent of converted CO per 100



Yield of methanol as a function of Cs loading over the calcined-doped (■) and reduced-doped (●) binary Cu/ZnO catalysts

Figure 5-11. Yield of Methanol as Function of Cs Loading

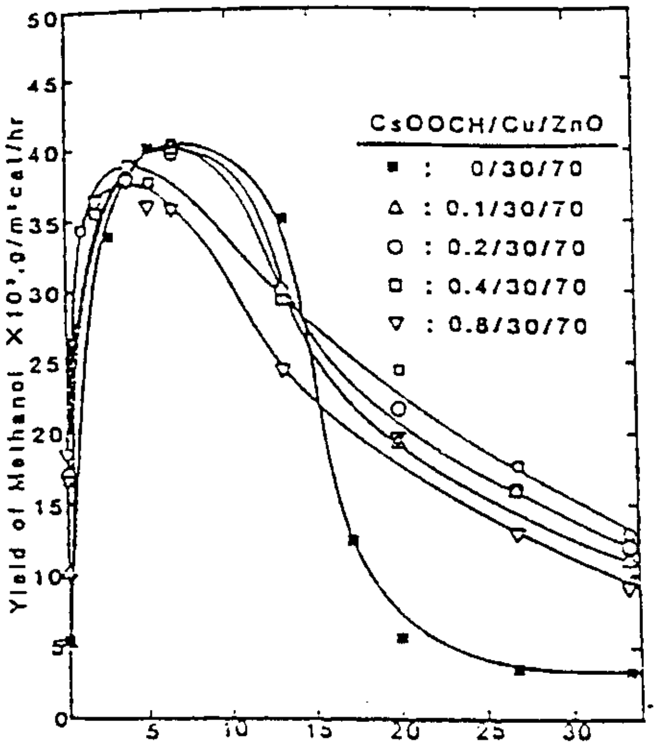


Figure 5-12. **Yield of Methanol as Function of Water Injection Rate**

hours has been established in a copper-lined reactor with carefully pre-purified gases. No deactivation rates were reported for the Cs/Cu/ZnO/(Cr_2O_3) catalysts under methanol synthesis conditions with variable concentrations of CO_2 in the SG.

5.3.1.4 Chemistry and Mechanism of Methanol Synthesis

The development of modern methanol synthesis technology has involved some seven decades of inventions, gradual improvements of catalysts, mechanistic work, and engineering design. The historic development was outlined in Section 5.3.1.1. Particular attention has been paid to the copper-based catalysts which are a key part of the most active and selective methanol synthesis technologies practiced today. New inventions are still occurring with copper catalysts and with copper-free catalysts in the area of both heterogeneous and homogeneous catalysis. It is desirable for methanol synthesis, as it is for any other process of importance, to resolve the chemical mechanism of key reactions, to analyze the intermediates, and to determine the functions of the individual catalyst components that steer the reactions to the most selective and efficient path. Finally, it is desirable to relate this mechanistic information to formal kinetics that could be used in process design.

Several reviews have been published on the mechanism of methanol synthesis over the copper-based catalysts only. The early, primarily kinetic studies of methanol synthesis were reviewed by Natta in 1955 (39), the mechanistic work by Kung in 1980 (74), the characteristics of the Cu/ZnO/M_xO_y catalysts along with the available mechanistic information by Klier in 1982 (38), new results on CO_2 versus CO hydrogenation and the role of metallic copper over the industrial Cu/ZnO/Al_2O_3 ICI catalysts by Chinchen et al. in 1987 (58), and most recently a comprehensive analysis of the current understanding of the copper-based catalysts by Bart and Sneeden (41), also in 1987. Subsequently and concurrently, a large number of papers have emerged that indicate that the mechanism and the kinetics of methanol synthesis are complex, may not be identical for different catalysts, and vary considerably with reaction conditions.

The reactions that result in the first C-H bond formation have been proposed to be

$$CO + H^{\ominus} \rightarrow \underset{\text{formyl}}{HCO^{\ominus}} \qquad [10]$$

$$CO + OH^{\ominus} \rightarrow \underset{\text{formate}}{HCOO^{\ominus}} \qquad [11]$$

$$CO_2 + H^{\ominus} \rightarrow \underset{\text{formate}}{HCOO^{\ominus}} \qquad [12]$$

Formyl may be formed directly from CO/H_2 or by hydrogenation of the formate. Both the formate and the formyl may be hydrogenated to methoxide

$$HCOO^{\ominus} + 2H_2 \rightarrow CH_3O^{\ominus} + H_2O \qquad [13]$$

which is then hydrogenated or hydrolyzed to form methanol. Formate and methoxide are readily detected under reaction conditions by IR spectroscopy (75-77), and formyl has been reported to form on co-adsorption of CO and H_2 over the Cu/ZnO catalysts (78). Initially, a hydroxycarbene route

$$CO + H_2 \rightarrow \underset{\text{hydroxycarbene}}{H\underset{\|}{C}OH} \qquad [14]$$

was postulated (81), but later it was pointed out that the catalyst would have to lower the 200-kJ/mol thermodynamic barrier of hydroxycarbene formation for this path to be effective (76).

With the help of labeled compounds, attempts have been made to resolve the proportion with which the different mechanisms operate. Takeuchi and Katzer (79) used a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$ that produced $^{13}CH_3{}^{16}OH$ and $^{12}CH_3{}^{18}OH$, but not $^{13}CH_3{}^{18}OH$ and $^{12}CH_3{}^{16}OH$, methanol over Rh/TiO_2 catalyst. This result favors the formyl path [8] and rules out the formate paths [11] and [12] for the Rh/TiO_2 catalyst under the conditions employed. However, the Cu/ZnO catalysts promote a rapid scrambling of $^{13}C^{16}O$ and $^{12}C^{18}O$ that is accelerated by preadsorbed water (80). This isotope flow is consistent with a reversible course of the formate mechanism [11]. To establish the kinetic role of water in methanol synthesis via route [11], Vedage et al. (80) injected D_2O into the CO/H_2 mixture to obtain methanol singly deuterated on the CH_3 group, $CH_2DO(H,D)$. Quantitative evaluation of the isotope flow led to the conclusion that reaction [11] accounted for at least 65 percent of the methanol synthesis from CO/H_2 + H_2O, again under the conditions employed in Reference 80.

Evidence for path [12] that utilizes CO_2 as the primary reactant has been obtained by hydrogenating $^{12}CO/^{14}CO_2$ and $^{14}CO/^{12}CO_2$ mixtures to methanol (81-83). For example, with $^{12}CO/^{14}CO_2$ mixtures, the ^{14}C label appeared in the product methanol for a large range of CO/CO_2 ratios, and a quantitative analysis of ^{14}C as a function of the flow rate of the reactants over the catalyst led to the conclusion that CO_2 hydrogenation is the exclusive primary path to methanol under the industrial conditions (temperature 250°C, pressure 40-50 atmospheres, and GHSV range of 10,000 - 120,000 hour^{-1}) that are utilized with the ICI Cu/ZnO/Al_2O_3 catalyst (86). In an earlier paper (84) the first step of CO_2 hydrogenation was proposed to be a formate-forming reaction between adsorbed CO_2 and hydrogen. Thus, based on the evidence utilizing the $^{13}C^{16}O$ + $^{12}C^{18}O$ mixtures, D_2O, and $^{14}CO_2/^{12}CO$ and $^{12}CO_2/^{14}CO$ mixtures as reactants, paths [10] - [12] are all feasible, but their dominance is dictated by the catalyst and the reaction conditions.

Reaction [11] is well known to occur under mild conditions even in aqueous solutions of alkali hydroxides (85). The details of this reaction have recently been investigated by reaction path calculations

(86,87) with the result that a facile nucleophilic attack of CO

$$\mathrm{HO}^{\ominus} + \mathrm{CO} \;\text{-->}\; \underset{(\mathrm{I})}{\overset{\ominus}{\overline{\mathrm{H\text{-}O\text{-}C\text{-}O}}}} \qquad [15]$$

is followed by an activated hydrogen transfer

$$\underset{(\mathrm{I})}{\overset{\ominus}{\overline{\mathrm{H\text{-}O\text{-}C\text{-}O}}}} \;\text{-->}\; \underset{(\mathrm{II})}{\mathrm{HCOO}^{\ominus}} \qquad [16]$$

as represented in Figure 5-13, where T is the transition state. The stable structures of the metalloformate (I), formate (II), and the transition state (T) are shown in the figure.

The reaction [11] has been documented by Bogdan (87) using the Cu/ZnO and CsOH-doped Cu/ZnO catalysts. The IR spectrum of the formate formed from a surface hydroxyl and CO on the Cu/ZnO catalyst is shown in Figure 5-14a and that of formate on CsOH/Cu/ZnO catalyst in Figure 5-14b.

A formate specifically bonded to the Cs^+ ions is documented by the comparison of the spectrum in Figure 5-14b with reference spectra of HCOOCs. The facile formation of surface HCOOCs from CsOH and CO led Klier and coworkers to the probing of CsOH/Cu/ZnO and later HCOOCs/Cu/ZnO catalysts for methanol synthesis (71) and the WGS reaction (73). The promotion by Cs of the Cu/ZnO catalyst for methanol is shown in Figure 5-11.

As already mentioned, the promotion of the Cu/ZnO catalysts for methanol is ion specific as Cs>Rb>K>Na,Li (70), in the same order as the basic strength of the counterion of the surface alkali cation such as OH^-. The dependence of methanol activity on the concentration of the alkali surface dopant shown in Figure 5-11 has been explained as follows. The catalyst is bifunctional and contains a basic component (e.g., CsOH) that enhances activation of CO by reaction [11] and a hydrogenation component (Cu/ZnO) that activates hydrogen for the conversion $HCOO^-$ -> CH_3O^-. The maximum methanol yield is obtained when the CO- and H_2-activating components are balanced. Although no calculations have been performed for the CO_2 hydrogenation path [12], it can be anticipated that this reaction will occur by a nucleophilic attack on the electropositive carbon of the (adsorbed) CO_2 molecule by a surface hydride with the

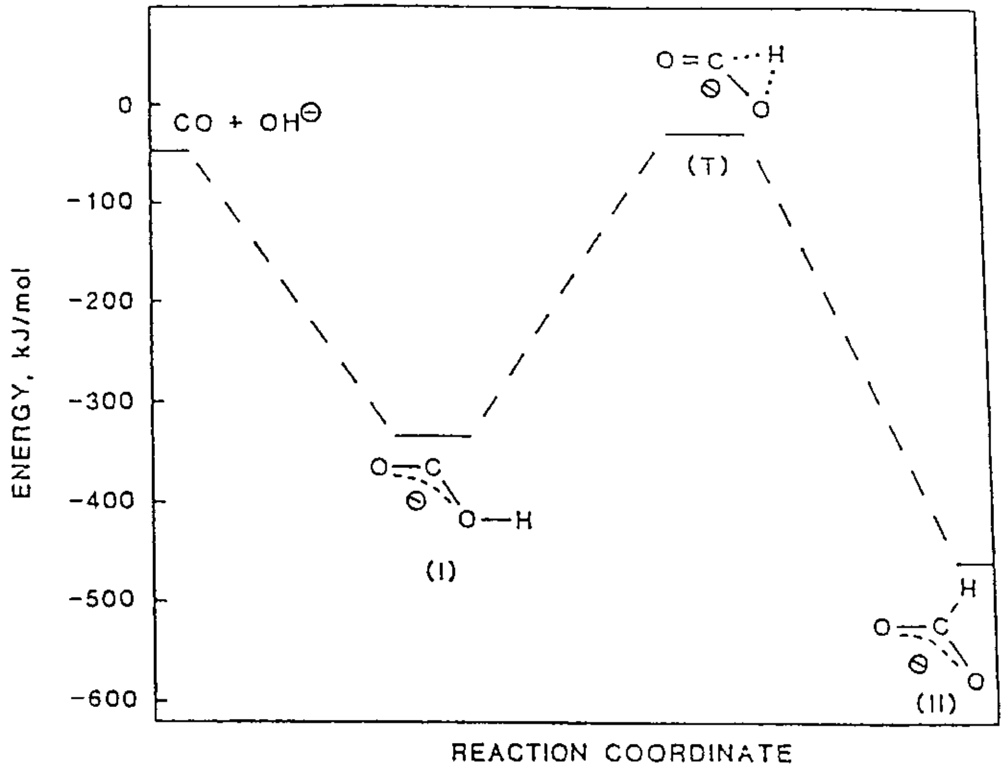
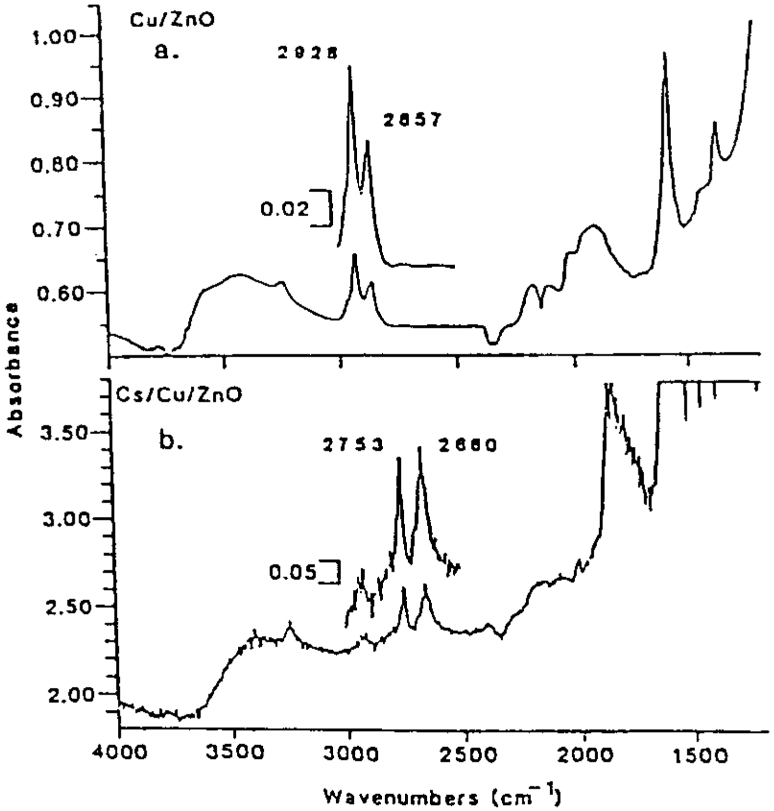


Figure 5-13. MNDO Energy Diagram for Reaction of Carbon Monoxide with Hydroxide to Form Formate



Infrared spectra of a) Cu/ZnO = 5/95 mol% and b) Cs/Cu/ZnO (50% surface coverage with cesium) obtained at 200°C and ambient pressure after carrying out methanol synthesis for 2 hr at 50 atm with H_2/CO = 0.50 synthesis gas.

Figure 5-14. Infrared Spectra

generation of surface formate $HCOO^-$. The hydride may also nucleophilically attack CO with the formation of surface formyl by surface reaction [10]. ICI researchers (88) have yet another picture in which the CO_2 molecule is adsorbed as $CO_2^{\ominus}$ and is attacked by "neutral" surface hydrogen atom to form the formate [17],

$$H_{(ads)} + CO_2^{\ominus} \rightarrow HCOO^{\ominus} \qquad [17]$$

The adsorbed hydrogen was presumed to be located on the metallic copper component of the $Cu/ZnO/Al_2O_3$ catalyst, although the same group recently reported, in the discussion at the 9th ICC, a large amount of hydrogen stored in the zinc oxide phase (89).

A pattern of base co-catalyzed CO hydrogenation, similar to that occurring over the copper-based catalysts, that gives a maximum methanol yield at an optimum alkali concentration was obtained with the alkali/MoS_2 catalysts as exemplified in Figure 5-21 in Section 5.3.2 on higher-alcohol synthesis. The catalyst requires a simultaneous presence of the alkali component and the MoS_2 component for developing alcohol synthesis activity. Consistent with the picture obtained for the Cs/Cu/ZnO catalysts, the Cs/MoS_2 catalyst appears to be a combination of a basic (CsOH) and a hydrogenation (MoS_2) component. The amount of the alkali component necessary to develop a maximum activity in MoS_2 is significantly larger than that in the Cs/Cu/ZnO catalyst because the alkali compounds agglomerate into approximately 20-nm particles which are in contact with the low-energy non-polar MoS_2 surface (90), while they are molecularly dispersed in a submonolayer on the polar Cu/ZnO surface (70).

A further example of a bifunctional base-hydrogenation catalyst for methanol that has recently been reported by Union Carbide (60) was presented in Section 5.3.1.3. This homogeneous catalyst consists of a Cu^+ compound and an alkali methoxide, and the hydrogenation component is believed to be the copper hydride CuH. The alkali methoxide may then serve as a base that activates CO by a nucleophilic attack [18] analogous to reaction [11] followed by hydrogenation of the metallocarboxylate III.

$$CH_3O^{\ominus}Na^{\oplus} + CO^{-} \rightarrow \underset{(III)}{CH_3OCO^{\ominus}Na^{\oplus}} \qquad [18]$$

The metallocarboxylate is then attacked by methanol to generate methyl formate and regenerate sodium methoxide [19].

$$CH_3OCO^{\ominus}Na^{\oplus} + CH_3OH \rightarrow CH_3O^{\ominus}Na^{\oplus} + HCOOCH_3 \qquad [19]$$

Methyl formate is then hydrogenated by the cuprous hydride [20].

$$HCOOCH_3 + 2H_2 \xrightarrow[CuH]{} 2CH_3OH \qquad [20]$$

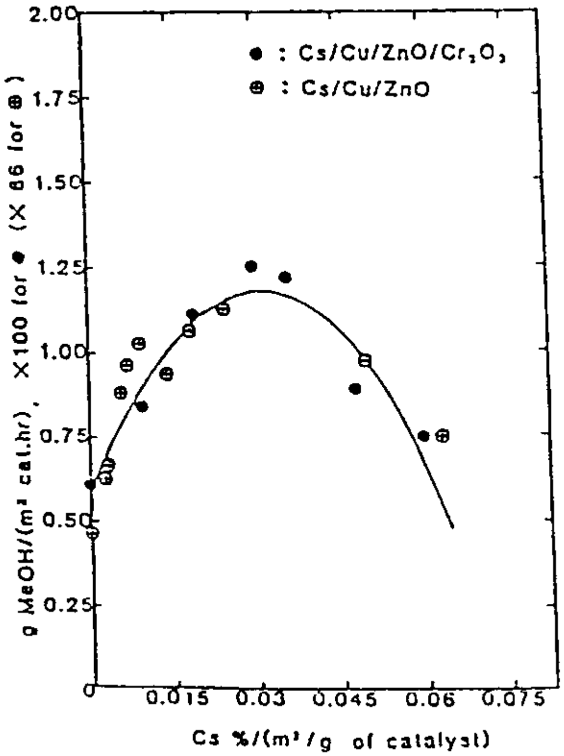
In summary, several new successful synthesis catalysts for methanol synthesis from CO and H_2 appear to be bifunctional, consisting of a basic component and a hydrogenation component. The $Cu/ZnO/Al_2O_3$ catalysts appear to hydrogenate CO_2 preferentially under industrial conditions. All three initial C-H forming reactions [10] - [12] have been found plausible for different catalysts and different sets of conditions. One major remaining task is to translate the mechanistic input into kinetic equations that describe the behavior of the synthesis reactions [1] - [3] in a wide range of conditions for each specific catalyst.

For a limited range of conditions and CO/H_2 synthesis gas only, methanol synthesis has been modeled as a function of surface Cs concentration for the Cs/Cu/ZnO and $Cs/Cu/ZnO/Cr_2O_3$ catalysts (72). The differential equation describing the cesium concentration dependence of the synthesis is

$$r_M = (k_1\theta_{Cs}\theta_{H2}(1-\theta_{Cs}) + k_0\theta_{CO}\theta_{H2}{}^{n}(1-\theta_{Cs}))(1-R/K_{eq})S \qquad [21]$$

The theoretical curves obtained by the best fit to the experimental methanol synthesis rates at 250°C and 75 atmospheres at $H_2/CO = 2.33/1$

Figure 5-15. **Correlation of Specific Methanol Activity as a Function of Normalized Cesium Surface Concentration**



Correlation of specific methanol activity as a function of normalized cesium surface concentration of Cs/Cu/ZnO (⊕) and Cs/Cu/ZnO/Cr_2O_3 (●) catalysts tested at 250°C and 75 atm with H_2/CO = 2.33 synthesis gas at GHSV = 6120 (unsupported) and 10,000 (Cr_2O_3-supported) ℓ(STP)/kg catal/hr.

are shown in Figure 5-15. The key term in Equation [21] proportional to $\Theta_{Cs}(1-\Theta_{Cs})$ reflects the bifunctionality of the synthesis, the rate of activation of CO being proportional to Θ_{Cs} and that of hydrogen to the free Cu/ZnO surface through $(1-\Theta_{Cs})$.

Both the methanol synthesis [1] and the side reactions occurring therein display chemical patterns that are indicative of the kinetic and mechanistic significance of an aldehydic C_1 intermediate. This intermediate may be formed directly as formyl by Reaction [10] but where the formate routes [11] and [12] are more efficient as on the $Cu/ZnO/M_2O_3$ catalysts, by a subsequent reduction

$$HCOO^{\ominus} + H_2 \rightarrow H_2O + HCO^{\ominus} \qquad [22]$$

or

$$HCOO^{\ominus} + {}^{1}/2\ H_2 \rightarrow \underset{\text{dioxymethylene}}{H_2COO^{\ominus}} \qquad [23]$$

Formyl $HCO^{\ominus}$ has been represented in Reactions [10] and [22]. Other forms of an aldehydic intermediate that have been proposed include-bonded formaldehyde, its isomer hydroxycarbene, and dioxymethylene which, if bonded to surface cation(s), is an anion of hydrated formaldehyde $H_2C(OH)_2$. IR spectra in the 2700-3000 cm^{-1} region have been interpreted (91) as vibrational transitions of the CH_2 group of dioxymethylene or adsorbed formaldehyde, but the evidence for hydroxycarbene is lacking.

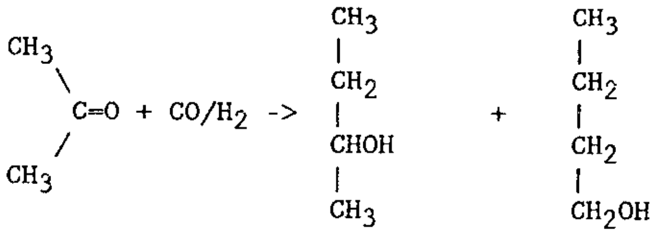
A number of chemical trapping reactions provide support for the aldehydic C_1 intermediate. Vedage et al. (92) utilized the reaction

$$R_1R_2NH + CO/H_2 \rightarrow R_1R_2NCH_3 + H_2O \qquad [24]$$

in which the CH_3 group of the product amine $R_1R_2NCH_3$ was synthesized via R_1R_2NH amine-C_1 aldehyde coupling. Deluzarche et al. (93) used methyl iodide to trap formyl with the result

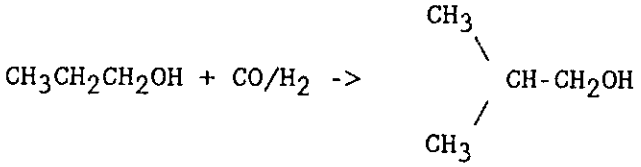
$$CH_3I + CO/H_2 \rightarrow CH_3CHO\ (+\ I^{\ominus}_{ads}) \qquad [25]$$

and Young et al. (72) used various alcohols and ketones, e.g.,



[26]

$$(CH_3)_2C{=}O + CO/H_2 \rightarrow CH_3\text{-}CH_2\text{-}CHOH\text{-}CH_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$$



[27]

$$CH_3CH_2CH_2OH + CO/H_2 \rightarrow (CH_3)_2CH\text{-}CH_2OH$$

to demonstrate that the addition of the C_1 intermediate formed from CO/H_2 occurred preferentially in the β position of the C_n alcohol of ketone. Such a reaction is typical of aldol condensation followed by hydrogenation, with some specific features regarding oxygen retention that are discussed in detail in Section 5.3.2.2. The high rates with which all of these reactions occur over the copper-based catalysts under synthesis conditions indicate that the C_1 aldehydic intermediate is a kinetically and mechanistically important reactive species.

As the side products are formed, particularly under the higher-alcohol synthesis conditions, higher aldehydes and ketones become important as chain building blocks, giving rise to a regular synthesis pattern of aldehyde coupling reactions that are reflected in the characteristic higher oxygenate product composition. The chemistry of these C_2+ syntheses is described in Section 5.3.2.

5.3.1.5 Research Trends

Research trends in methanol synthesis appear to be motivated by the desire to

- understand the function of the existing highly active and selective low-pressure methanol synthesis catalysts,

- understand the mechanisms of CO and CO_2 hydrogenation to methanol over a variety of catalysts based on copper, Group VIII metals, sulfides, and their combination with alkali compounds,
- develop a highly selective and stable homogeneous catalyst for methanol,
- develop reliable and reproducible methods for catalyst preparation based on detailed understanding of the solid state and surface chemistry of heterogeneous catalysts, and solution chemistry of homogeneous catalysts, and
- develop a high degree of control of the water gas shift reaction and its reverse as it occurs simultaneously with methanol synthesis from $H_2/CO/CO_2/(H_2O)$ SG.

Specific items that appear of interest are the following:

- Determine the active state of copper in heterogeneous and homogeneous copper-based catalysts and methods for optimizing its concentration (valence doping $Zn_2^{II} \rightarrow Cu^{I}Cr^{III}$, $Cu^{I}H$, Cu intermetallics).
- Further develop promising homogeneous catalysts for methanol, and invent novel ones.
- Develop active and selective heterogeneous catalysts for methanol based on alkali containing hydrogenation catalysts that are free of copper. An example of such catalysts that are not yet selective enough for methanol but show a good total oxygenate synthesis activity is the alkali/MoS_2 catalysts described in Section 5.3.2.2.
- Determine the long-term performance of the promising alkali/Cu/ZnO/Cr_2O_3 catalysts under methanol synthesis conditions and in the presence of CO_2.
- Determine the state of and resistance to various impurities, such as iron and nickel carbonyls and S-, Cl-, H_2O-, and CO_2-containing gases, in all heterogeneous and homogeneous catalysts that show promise for industrial applications.