- Stabilize the catalysts by properly chosen, preferably heat conducting, supports. Under the HAS conditions, this does not appear to be a problem for the MoS_2-based catalysts which excel by extraordinary ruggedness and stability. On the contrary, the alkali-doped copper-based catalysts exhibit a strong dependence of selectivity on the choice of support such as Al_2O_3, Cr_2O_3 or Ga_2O_3 (105).

- Investigate further the influence on selectivity and activity of oxide (Mo, Zn and others) components in the Group VIII (particularly Rh) metal-mixed oxide catalysts.

- Investigate the effects of alkali promoters on the performance in HAS of the very highly active copper-based catalysts derived from intermetallics described in Section 5.3.1.

- Explore and investigate novel low-temperature, low-pressure catalysts for HAS, for both heterogeneous and homogeneous catalysts.

5.3.3 Water Gas Shift (WGS) Technologies

The WGS technologies are well-developed and commercially proven. Kuo (152) has given a concise review of WGS catalysts and chemistry. The high-temperature shift (440-700°C) Cr-Fe oxide or Zn-Cr oxide catalysts, low-temperature shift (230-350°C) Cu-Zn-Al or Cu-Cr oxide catalysts, and raw-gas shift (180-550°C) Co-Mo sulfide catalysts and their performance were also summarized in the 1987 DOE Coal Gasification report (1). The water gas shift reaction [3] has been proposed to occur by two

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad [3]$$

principal mechanisms, the redox mechanism [25], where M stands for an

$$\begin{aligned} &CO + O_{(ads)}\text{-}M \rightarrow CO_2 + M \\ &H_2O + M \rightarrow O_{(ads)}\text{-}M + H_2 \end{aligned} \qquad [50]$$

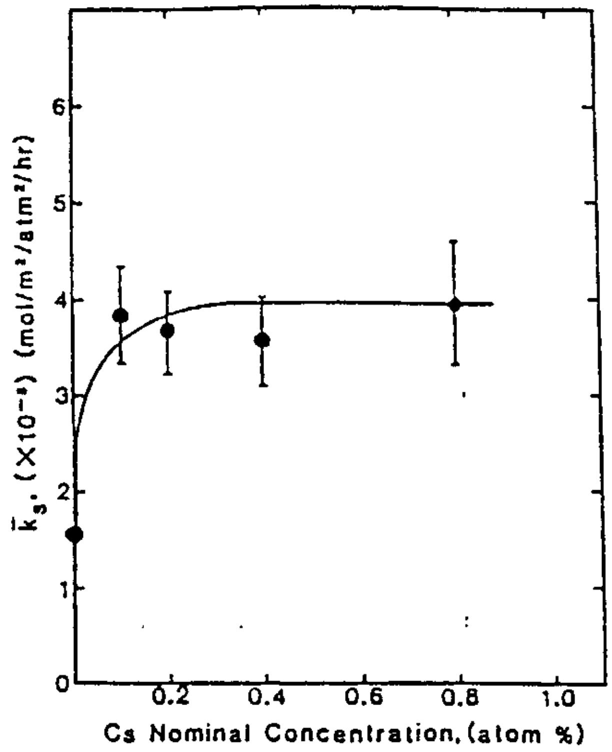
oxidizable free site on the catalyst surface and $O_{(ads)}$ for the adsorbed oxygen atom generated by oxidation of the free site by water, and the associative formate mechanism [51], in which the first step is identical

$$CO + HO^{\ominus}{}_{(ads)} \rightarrow HCOO^{\ominus}$$
$$2HCOO^{\ominus} \rightarrow 2CO_2 + H_2 + 2e^- \qquad [51]$$
$$2H_2O + 2e^- \rightarrow 2HO^{\ominus}{}_{(ads)} + 2H_2$$

with the first step [4] in methanol synthesis discussed in Section 5.3.1.4 and is followed by the decomposition of the formate $HCOO^{\ominus}$ and reoxidation of the catalyst by water. The formate mechanism [51] therefore also involves partial redox reactions, but the difference between [51] and [50] is in the mechanism of the formation of CO_2, via reaction of CO with surface hydroxyls [51] or directly with chemisorbed oxygen [50].

ICI researchers presented arguments that the low-temperature $Cu/ZnO/Al_2O_3$ WGS catalysts operate via the redox mechanism [50] where M is the copper metal surface atom (83). On the other hand, Klier et al. (73) improved the WGS activity of the Cu/ZnO catalysts by cesium hydroxide or cesium formate doping, taking the approach that the formate mechanism [51] is operating, at least on the alkali-doped catalyst. The WGS rates were increased by a factor up to 2.3 by additions of small amounts (0.1-0.8 wt percent) of cesium compound to the Cu/ZnO catalyst, as shown in Figure 5-29. The WGS rates were determined concurrently with methanol synthesis and not at low pressures, at which the WGS takes place without methanol synthesis. Also, the long-term stability of the Cs/Cu/ZnO catalysts and the effects of supports such as Cr_2O_3 or Al_2O_3 were not determined. However, the heavy alkali doping has been demonstrated as a promising route to improved low-temperature WGS catalysts.

Alkali doping also imparts a significant WGS activity on the MoS_2 catalysts, and the chemistry of WGS in this system has yet to be resolved. If the formate route [51] operates, all reactions may occur on the alkali component with the electrons released in the second step and consumed in the third step being accepted and re-supplied by MoS_2.



Average forward WGS rate constants $\bar{k}_S$ (ordinates) as a function of cesium concentration (abscissas) in the HCOOCs/Cu/ZnO catalysts for the pressure 75 atm, temperature 235 °C, and $H_2/CO = 2.33$ synthesis gas.

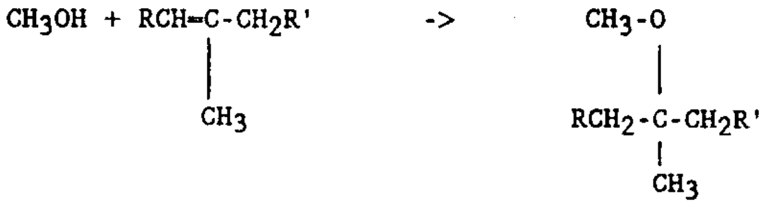
Figure 5-29. Average Forward WGS Rate Constants

In conclusion, although the WGS technology is mature and is in a wide commercial use, improvements are still possible and being reported, and certainly a great deal of effort is needed to unambiguously resolve the WGS mechanism for each individual catalyst.

5.3.4 The Methyl Tertiary-Butyl Ether (MTBE) and Tertiary-Amyl Methyl Ether (TAME) Technology

5.3.4.1 Introduction and Historic Notes

MTBE and TAME are produced by reactions of methanol with tertiary olefins,



$$CH_3OH + RCH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2R' \; -> \; RCH_2{-}\overset{\displaystyle CH_3{-}O}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{-}CH_2R' \qquad [52]$$

where R=R'=H for isobutene that gives rise to MTBE, and R=CH_3, R'=H for 2- methyl-2-butene (isoamylene) and R=H, R'=CH_3 for 2-methyl-1-butene, both of which give rise to TAME. The ethers MTBE and TAME constitute the fastest growing use of methanol, along with petroleum-derived hydrocarbons C_4H_8 or C_5H_{10}, in the U.S. and Europe (153 - 157). MTBE and TAME are rated with octane RON/MON 118/101 and 105-122/96-105, respectively. When blended into gasoline at a level of 10 percent, these ethers increase the RON and MON by 2-3 units (153). MTBE and TAME can be used as octane enhancers by themselves but also as cosolvents for blends of methanol in gasoline, since methanol is less expensive and has higher octane than both gasoline and MTBE or TAME.

The world's MTBE and TAME capacity has grown significantly recently, the newly plants built, under construction, or engineered in 1986-1988 totaling more than 4.7 billion kg in annual capacity (37).
Between 1986 and 1987 the world's production of MTBE alone rose from the 24th to the 18th place among organic chemicals to 1.5 billion kg in 1987, averaging 50.7 percent annual growth (158). Currently, MTBE occupies approximately 50 percent of the oxygenate blending agents market, and its

use is rising. However, El Sawy (101) anticipates constraints for future increases of MTBE production in the limited supply of isobutene and in a cost factor (1.4 compared to methanol and 1.12 compared to higher alcohols) that will make alcohol fuel blends economically competitive with MTBE and possibly reverse the trend. A similar consideration applies to TAME.

Currently, in the production of MTBE (TAME), one carbon atom originates from methanol that could be made from coal-derived SG (but most of which is made today from natural gas or naphtha), and four (five) carbon atoms originate from petroleum in the form of specific olefins as indicated by Equation [52]. Thus, MTBE and TAME production still relies on petroleum (at least to 80-83 percent) as a raw material, and currently there are no indications of switching to coal resources. There are known chemical paths to MTBE, however, that permit the total use of coal-derived SG as a raw material, e.g., via isobutanol (2-methyl-1-propanol) directly synthesized from SG as shown in Section 5.3.2.1. Isobutanol can then be catalytically dehydrated to isobutene and MTBE synthesized by the process represented by reaction [52] with R=R'=H. Some other approaches are mentioned in Section 5.3.4.3.

MTBE was introduced commercially in Europe in 1973 using Snamprogetti technology (153, 157, 159). In the U.S. after the first MTBE plant was built in 1979, 14 plants were running in 1983, and the capacity is growing worldwide.

5.3.4.1 The MTBE and TAME Technology

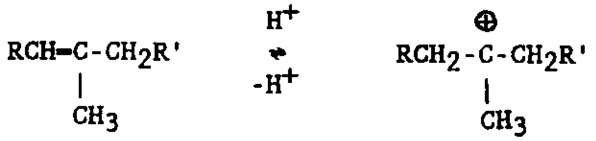
J.D. Chase reviewed the basic features of the MTBE and TAME technology in 1983 (153). These ethers are produced with high (97-99 percent) selectivity by solid acid-catalyzed coupling reactions [52] under mild conditions at 0.7- 1.4 MPa, 70-110°C, and a liquid hourly space velocity of 13.5 (based on the olefin), with conversions of 86-96 percent. The STY's are also high, being in the range of 0.022-0.05 kg of isobutene consumed per kg catalyst per hour in MTBE manufacture. MTBE is produced at an 85-percent higher initial rate than TAME under comparable conditions.

In the Gulf Canada process (161) methanol is used in two-fold excess to the stoichiometric amount required by reaction [52]. The unreacted methanol is removed by adsorption in glycol rather than by distillation, which is rendered impractical due to the existence of methanol-C_4 azeotropes. A schematic flow sheet for the Gulf Canada MTBE process is shown in Figure 5-30. A patent covering the Gulf Canada combined process for MTBE and TAME was awarded in 1980 (162). The Institute Francais du Petrol (IFP) has a process utilizing an alternative approach of separate reactors for MTBE and TAME (163). The largest TAME plant, under construction at Feyzin, France, utilizes the IFP technology and the largest MTBE plant, at Al Jubail, Saudi Arabia, the Snamprogetti technology.

The catalysts for both the MTBE and the TAME manufacture are cation exchange resins that are exchanged with protons to impart surface acidity (160, 164), and they are used in the liquid phase. Despite the fact that high synthesis rates, liquid-phase conditions, large catalyst particle sizes, and low temperatures are used, the process is believed to occur in the kinetic reaction regime and not to be mass-transfer limited. The reaction rate is first order in the tertiary olefin concentration and zero order in methanol when a stoichiometric excess of methanol is used. Thus, simple, efficient, and selective production processes exist for MTBE and TAME, and the underlying chemistry is well understood in terms of carbenium intermediates as discussed in the next section.

5.3.4.3 Chemistry and Mechanism

The tertiary olefins involved in reaction [52] readily make tertiary carbenium ions through the equilibrium [53], and these react with methanol



$$RCH{=}\underset{\substack{|\\CH_3}}{C}{-}CH_2R' \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} RCH_2{-}\underset{\substack{|\\CH_3}}{\overset{\oplus}{C}}{-}CH_2R' \qquad [53]$$

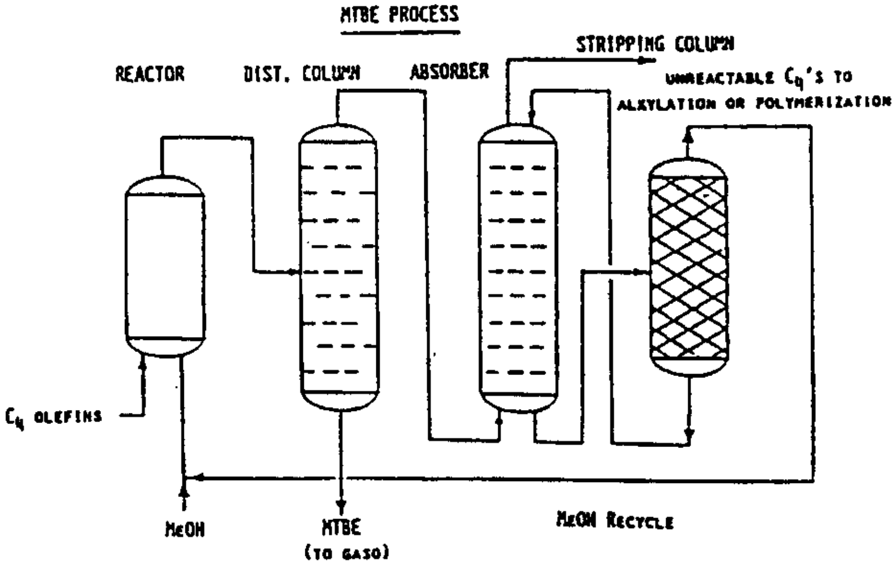
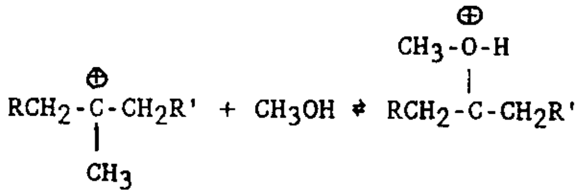


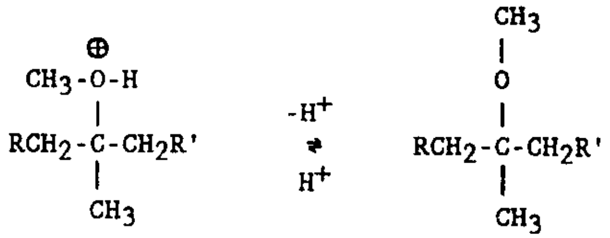
Figure 5-30. A Schematic Diagram of the Methyl Tertiary-butyl Ether (MTBE) Process

to form an oxonium intermediate [54] which upon the loss of proton converts to the product ether, [55].



$$RCH_2-\underset{CH_3}{\overset{\oplus}{C}}-CH_2R' + CH_3OH \rightleftharpoons RCH_2-\overset{\overset{\oplus}{CH_3-O-H}}{\overset{|}{C}}-CH_2R'$$

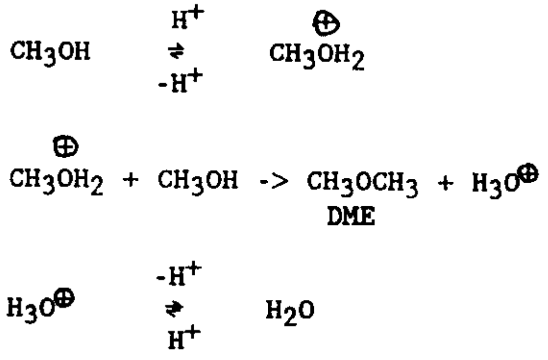
[54]



$$RCH_2-\overset{\overset{\oplus}{CH_3-O-H}}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2R' \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} RCH_2-\overset{\overset{CH_3}{|}}{\overset{O}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}}-CH_2R'$$

[55]

Reactions [54] and [55] may occur in a concerted fashion. Competing undesirable side reactions may involve acid-catalyzed olefin oligomerizations that also occur via carbenium intermediates, and acid-catalyzed dehydration of methanol to dimethyl ether (DME) that occurs via an oxonium mechanism [56].



$$CH_3OH \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} \overset{\oplus}{CH_3OH_2}$$

$$\overset{\oplus}{CH_3OH_2} + CH_3OH \rightarrow \underset{DME}{CH_3OCH_3} + H_3O^{\oplus}$$

$$H_3O^{\oplus} \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} H_2O$$

[56]

The extent to which the side-product olefin oligomers and DME appear in the product has not been reported in detail, although the selectivities for the main reaction [52] are known to have attained 97-99 percent at conversion levels up to 96 percent.

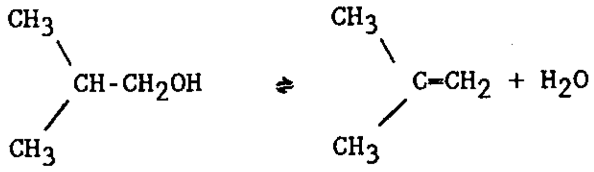
5.3.4.4 Novel Synthesis of Octane-Enhancing Ethers from Alcohols

A direct coupling of alcohols to ethers by the general reaction [57] has recently been reported to occur on superacid resins (165). Here the

$$CH_3OH + ROH \rightarrow CH_3OR + H_2O \qquad [57]$$

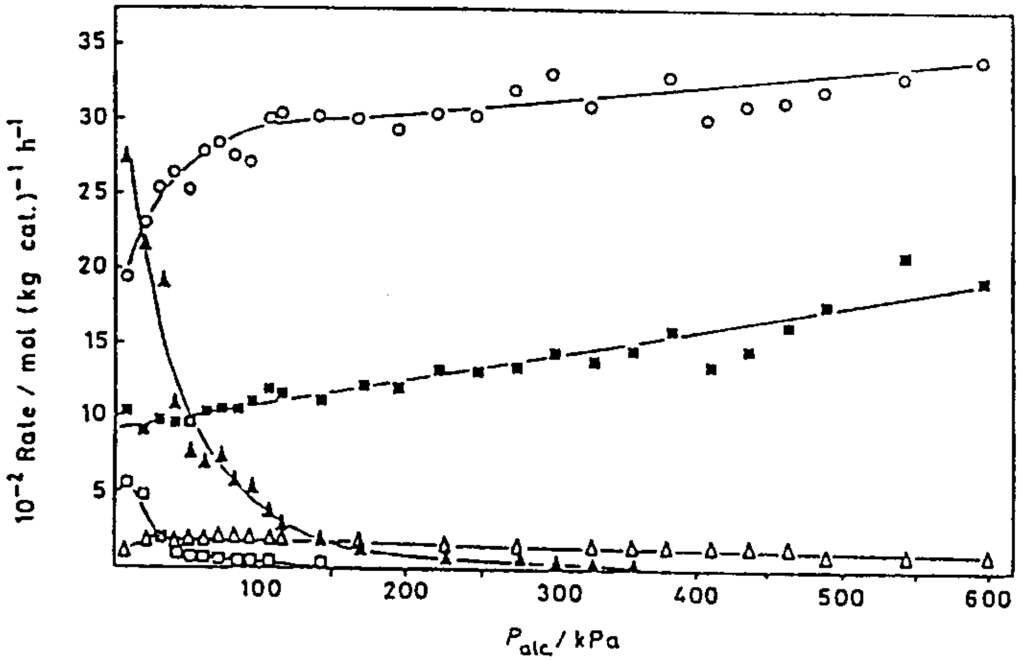
source of the methyl-alkyl ether is methanol and an alcohol ROH (R = higher alkyl) instead of methanol and an olefin in reaction [52]. Research into the synthesis [57] was motivated by the fact that methanol-isobutanol (R = 2-methyl-1-propyl) mixtures can be synthesized directly from coal-derived SG, and therefore all carbons in the ether CH_3OR produced by reaction [57] would originate from coal.

When isobutanol was coupled as ROH with methanol over a Nafion-H resin, the ether produced was methyl-isobutyl ether (MIBE), or 1-methoxy-2-methyl propane, rather than MTBE, showing convincingly that reaction [57] did not proceed via dehydration of isobutanol to isobutene [58] followed by reaction [52] because in that case MTBE would be the



$$(CH_3)_2CH\text{-}CH_2OH \rightleftharpoons (CH_3)_2C{=}CH_2 + H_2O \qquad [58]$$

expected product. The formation of MIBE indicates a different mechanism involving oxonium or surface sulfate ester intermediates (165). The side products of the MIBE generating reaction [57] (with R = 2-methyl-1-propyl) are butenes, DME, di-isobutyl ether (DIBE) and octenes; the olefin formation can be suppressed by pressure. At pressures exceeding 0.4 MPa, the olefin formation is negligible at temperatures below 130°C. Interestingly, the mixed ether MIBE is preferred to DME and DIBE in the product as shown in Figure 5-31. The Nafion-H resin is stable up to 200°C. Steady yields of MIBE of 0.23 kg/kg cat/hour were obtained at a temperature of 160°C and a pressure of 7.6 MPa with 42 mol percent selectivity. The conditions for alcohol coupling [57], although mild in general terms applied to catalytic



Variation of product yield with alcohol mixture partial pressure at a steady-state reaction rate. Reactants, MeOH-Bu^{i}OH (2:1); alcohol feed, 15.59 mol (kg cat.)$^{-1}$ h^{-1}; N_2 feed, 186 mol (kg cat.)$^{-1}$ h^{-1}; catalyst (Nafion-H Micro-Saddles) wt., 1.0 g; *T*, 389 K. ○, MIBE; ■, Me_2O; ▲, butenes; □, octenes; △, Bu^i_2O.

Figure 5-31. Variation of Product Yield with Alcohol Mixture Partial Pressure

processes, are slightly more severe than for the methanol-olefin coupling [52], and the selectivities of the MIBE process [57] are lower than of the MTBE process [52].

The octane-enhancing value of MIBE has not been determined, and there are some reservations concerning the stability of MIBE upon long-term exposure to air. Therefore, it is likely the MTBE will remain the most attractive octane-enhancing ether. Should the coal technology of the future aim at MTBE from the coal-derived methanol-isobutanol mixture, the chemical path involving a catalytic dehydration of isobutanol [58] followed by the established MTBE technology (Section 5.3.4.2) appears more feasible.