Development of Methanol Decomposition Catalysts for Production of H₂ and CO

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Introduction

Emission from motor vehicles and electric power generation plants are two of the largest sources of air pollution. Since the passage of the Clean Air Act in the U.S. in 1990, efforts to reduce air pollution have been spread worldwide. Hydrogen is the cleanest fuel. However, hydrogen is difficult and costly to transport and to store. Methanol is considered as a renewable energy source and the best hydrogen carrier available today.[1]

The fuel cell technology is developing rapidly and has attracted wide interest for both electric power generation and electric vehicles. The steam re-forming of methanol to hydrogen and carbon dioxide is very promising as a hydrogen source for the fuel cell application.[2] Methanol can also be decomposed directly to CO and H₂. The decomposed methanol is a cleaner and more efficient fuel than gasoline and undecomposed methanol for internal combustion engines of automobiles.[3,4] Both decomposed methanol and re-formed methanol can also be used as a fuel for gas turbines at peaking demand of electricity.[5] Methanol reactions can provide a convenient and economical on-site source of CO and/or hydrogen for chemical processes and material processing.[6]

In the application in internal combustion engines as an example, methanol decomposition, an endothermic reaction, can be conducted by making use of engine exhaust heat, which increases the heating value of the fuel. However, because of the limited space in the engine compartment and limited temperature of the exhaust heat, especially at cold start, the methanol decomposition catalysts need to be active at low temperatures. Catalysts could be deactivated in a methanol decomposition environment.[7] Conventional Cu/ZnO-based methanol synthesis catalysts performed poorly in methanol decomposition.[8] The catalysts suffered from rapid deactivation. The

activity and stability have been two major challenges in the methanol decomposition reaction.

In the past 10 years, significant progress has been made in the above challenging areas. This Account discusses the chemistry and technology of the progress after briefly reviewing the applications of the methanol decomposition reaction.

Applications

Alternative Automobile Fuel. Although undecomposed liquid methanol is a promising automobile fuel, decomposition of methanol to CO and H₂ on board a vehicle (Figure 1) provides a fuel that is more efficient and cleaner than liquid methanol. Methanol decomposition is an endothermic reaction. The reaction heat can be provided by the engine exhaust gas. This recovers the waste heat and increases the heating value of the fuel. Like pure H₂, decomposed methanol has excellent properties for spark-ignition combustion. Internal-combustion engines running on decomposed methanol can be operated under leaner combustion than those on liquid methanol or gasoline and at higher compression ratios than those on gasoline. These further increase the thermal efficiency of the decomposed methanol fuel. Decomposed methanol could be up to 60% more efficient than gasoline and up to 34% better than undecomposed methanol.[3]

The decomposed methanol fuel that is rich in hydrogen and CO will burn much cleaner than the liquid methanol fuel. Lean and complete combustion will ensure low CO and hydrocarbon emissions. The formaldehyde emission will be improved. NO$_x$ emission will be greatly reduced because of lower combustion temperatures.

Experimental vehicles running on decomposed methanol have been operated by a number of organizations to demonstrate the feasibility and advantages of using decomposed methanol. For example, Karpuk and co-workers modified a Ford Escort and showed that, at a light engine load, decomposed methanol provided 17.7% lower fuel consumption and an order of magnitude reduction of NO$_x$ emission compared with lean-burning liquid methanol.[9] Researchers at the Solar Energy Research Institute (SERI) used a copper/zinc oxide-based catalyst to decompose methanol and fueled a 1980 Chevrolet Citation with the decomposed methanol.[5] The efficiency was more than 40% higher than for gasoline operation. Work at the Japan Automobile Research Institute also indicated high thermal efficiency and low exhaust emission levels during both transient and steady-state driving of a decomposed methanol-fueled car.[10]

Gas Turbines (High-Pressure Application). Methanol decomposition can also be driven by heat from gas turbine exhaust gas. This would increase the heating value and make decomposed methanol an attractive fuel for power plants at peaking demand of electricity.[3–5] Since most gas turbine units for electric generation operate at about 12–15 atm, the methanol decomposition needs to be run at about 15–20 atm. This is compared with an about 2 atm

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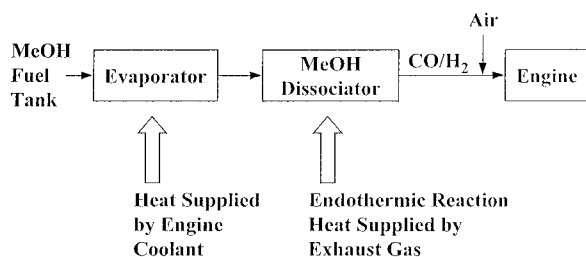
FIGURE 1. Methanol decomposition on board a vehicle.

operation pressure for the automobile application. The theoretical and experimental works to demonstrate the advantage and feasibility of the gas turbine application have been conducted by a number of organizations such as Westinghouse Electric Corp.,[11] the National Defense Academy,[12] and the Chugoku Electric Power Company of Japan.[13]

Fuel Cell Development. Because of their several advantages over conventional power generation units such as high efficiency, low pollution, low noise, modular construction, and short construction period, fuel cells are becoming promising new energy systems. Technology development in this area has been rapid. For example, Japan has initiated a national hydrogen energy program named World Network.[14] Under the program, one 5 MW and one 1 MW phosphoric acid fuel cell (PAFC) power plants were installed recently. The program will also design a 5 MW polymer electrolyte fuel cell (PEFC) dispersed power plant. The proton-exchanged membrane (PEM) fuel cell is suitable for application on vehicles. Fuel-cell-driven automobiles (prototype) have been on the road.[15] For example, the "neCarII" vehicle using a 50 kW PEM fuel cell was tested by the Daimler-Benz Co. The vehicle can travel at a speed of 110 km/h over 1000 km, a distance much longer than those of battery-powered vehicles. Many other companies have also had prototype fuel-cell vehicles such as Volkswagen, BMW, Siemens, Ballard (Canada), and the Chicago Transient Authority (three city buses powered by fuel cells).[15] Chrysler also studied fuel-cell-powered vehicles but used an alternative approach that used gasoline as a feedstock.[16]

On-Site Source of CO and/or H_2. The decomposition of methanol can also provide a convenient, economical, and clean source of CO and H_2 for applications in chemical processes (e.g., carbonylation, hydrogenation, and hydroformylation) and materials processing. As an on-site source of CO and H_2, it can be operated under mild conditions and produces no sulfur or soot. Syngas production using other hydrocarbons such as fuel oil and natural gas requires re-forming or partial oxidation at high temperatures.

Although the potential gain from implementation of methanol decomposition related technology is evident, successful development of efficient catalysts and reaction processes is crucial for the implementation of the technology.
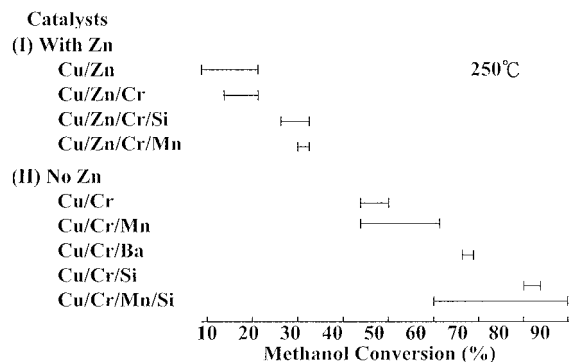

FIGURE 2. Conversion of methanol in methanol decomposition over a series of Cu-based catalysts at 250 °C and 2 atm after 16 h of reaction when semistable activity was achieved. Undiluted methanol vapor was fed to the reactor containing 1.8 g of a catalyst at 35 cm³ (STP)/min. Reprinted with permission from ref 8. Copyright 1995 Elsevier Science.

Methanol Decompositon Catalysts and Reaction

Cu/ZnO catalyats were systematically studied for methanol decomposition in some early work.[17,18] Subsequent studies on methanol decomposition largely concentrated on mechanistic and thermal desorption investigations.[19–24] ZnO or Cu/ZnO catalysts were often used because Cu/ZnO-based catalysts are industrial low-temperature methanol synthesis catalysts. However, it has been shown that these good methanol synthesis catalysts are not good methanol decomposition catalysts because of rapid deactivation in the methanol decomposition environment.[8,25,26]

Copper oxide-based catalysts are regarded as low-temperature methanol decomposition catalysts, typically operated at 200–275 °C. Zn/Cr catalysts are active around 350 °C. Pt group catalysts are high-temperature catalysts active at 400 °C or higher. Another branch of catalysts based on copper chloride were recently developed.[27] These catalysts are active at 350 °C or higher. Highly active low-temperature methanol decomposition catalysts based on Cu/Cr catalysts promoted with manganese, barium, or silicon oxide or alkali metal ions were developed.[8,28,29] The catalysts are much more active than conventional Cu/ZnO-based catalysts.

Activity and Selectivity. The methanol conversions at 250 °C over a series of Cu-based catalysts with and without ZnO are given in Figure 2 as an overview. A range of methanol conversion is indicated for each type of catalyst because various compositions, pretreatments, and preparation conditions were used. However, the effect of these factors was small compared to that of the type of catalyst.

Only cation and metal components of the catalysts are indicated. Oxygen is omitted. The catalysts were prepared by coprecipitation with Na_2CO_3. If Si is indicated as a component, a Cabosil silica was added to Na_2CO_3. Anhydrous liquid methanol was evaporated, and the undiluted methanol vapor was used as the feed in a continuous flow. The pretreatment of the catalysts included calcination in air at 300 °C for 3 h followed by reduction in 5% H_2/N_2 at 250 °C for 3 h. The reduction pretreatment reduced
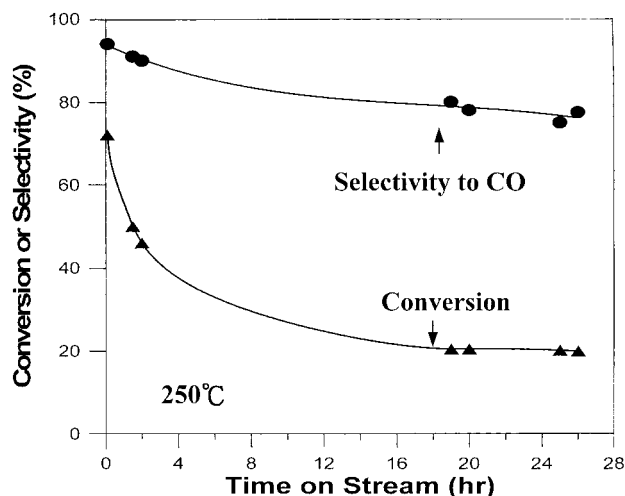
FIGURE 3. Deactivation of a Cu/Zn/Cr (27/63/10 by weight) catalyst in methanol decomposition. See Figure 2 for reaction conditions. Reprinted with permission from ref 8. Copyright 1995 Elsevier Science.
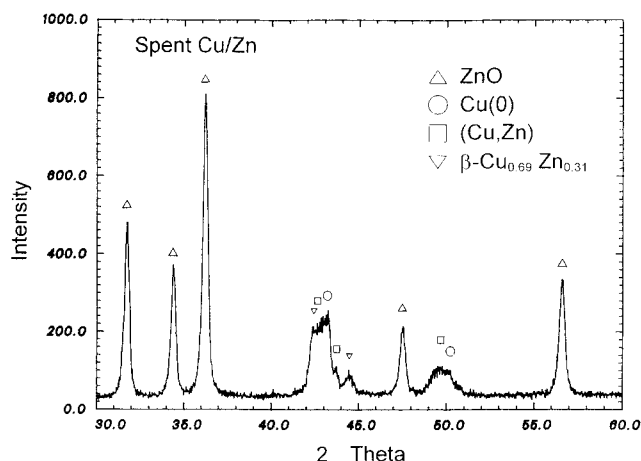

FIGURE 4. XRD pattern of a spent Cu/ZnO catalyst used in methanol decomposition. Reprinted with permission from ref 8. Copyright 1995 Elsevier Science.

oxidized Cu species to metallic Cu, but ZnO was maintained as the oxide. The intial activity of many Cu/Zn-based catalysts was also high. However, their activity dropped quickly in the first few hours of the reaction and reached a nearly steady activity after about 16 h (Figure 3). The initial rapid deactivation over Cu/Zn-based catalysts can be attributed to the dissolution of Zn into the Cu lattice.[8] The formation of Cu/Zn alloys was evidenced by XRD in spent Cu/Zn-based catalysts after methanol decomposition (Figure 4).

Figure 2 clearly shows that the activity of the Cu-based catalysts can be greatly enhanced by eliminating the ZnO component. The Cu-based catalysts without ZnO show much more stable activity and are therefore more active than those containing ZnO. Furthermore, Mn and alkaline earth elements such as Ba appear to promote the Cu-based catalysts for methanol decomposition. A small amount of silica (typically a few percent) further enhances the activity. The optimum activity was obtained at about 2.5 wt % Si.[8]

The product distribution of methanol decomposition over a Cu/Cr/Mn (NGC G89) catalyst is shown in Table

1.[29] A volume of 100 cm³ (STP)/min of methanol was fed over 0.6 g of catalyst at 1 atm. Similar to the Cu/ZnO catalyst, CO and H_2 were the major products at high methanol conversions. A significant amount of methyl formate was formed at low conversions. A small amount of dimethyl ether was produced, indicating the dehydration activity of this catalyst.

A study on the variation of the product distribution with space time at 150 °C indicated that methyl formate is a primary product at low methanol conversions and CO is produced at high conversions.[8] It was proposed that methyl formate is an intermediate in methanol decomposition as shown in eq 1.[26] It was also proposed that

$$2CH_3OH \rightarrow HCOOCH_3 + 2H_2 \rightarrow$$
$$CH_3OH + CO + 2H_2 \quad (1)$$
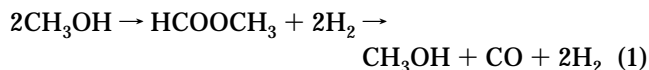
methyl formate was formed via a formaldehyde intermediate as indicated in eqs 2 and 3.[30]

$$CH_3OH \rightarrow CH_2O + H_2 \quad (2)$$

$$2CH_2O \rightarrow HCOOCH_3 \quad (3)$$
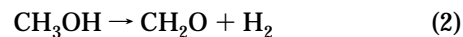
It was found that the production of dimethyl ether can be correlated with the composition of Cr in a variety of Cu-based catalysts.[8] This represents a major loss of the CO selectivity and would slightly reduce the heating-value gain of the fuel because of the exothermic dehydration reaction.

An attempt was made recently to tackle this problem and to further improve the catalyst activity[29] by the addition of alkali metal ions. A series of Cu/Cr/Mn/alkali metal catalysts were prepared by impregnating a Cu/Cr/Mn catalyst (NGC G89) with sodium or potassium nitrate solution. The modified Cu/Cu/Mn catalysts contain 2 wt % Na or K. The product distribution, methanol conversion, and selectivities to CO and H_2 over Cu/Cu/Mn, Cu/Cr/Mn/Na, and Cu/Cr/Mn/K are shown in Table 1.[29] The alkali metal containing catalysts have discernibly higher methanol conversion, higher selectivities to CO and H_2, and smaller amounts of dimethyl ether produced than the Cu/Cu/Mn catalyst at three indicated temperatures. Potassium gives stronger promoting effects than sodium. The neutralization of the acidity of chromia by alkali metal ion was also observed in alcohol synthesis where the formation of dimethyl ether was reduced, when Cs was added to a Cu/ZnO/Cr₂O₃ catalyst.[31]

How can alkali metal ions increase the catalyst activity in methanol decomposition? Table 2 shows that the Cu crystallite size determined by X-ray line broadening decreased with the concentration of potassium additive.[6] Consistently, the Cu surface area also increased with the potassium concentration. The Cu surface area was measured by the method[32,33] of surface oxidation of Cu by N₂O followed by temperature-programmed reduction. The initial CO yield also increased with the K concentration. These correlations strongly suggest that the potassium promoter enhances the Cu dispersion, which contributes to the increased activity in methanol decomposition. Other possible factors such as the oxidation state of

Table 1. Methanol Decomposition over Alkali Metal Promoted and Unpromoted Cu/Cr/Mn Catalysts

| reaction temp | catalyst | concn in the effluent (mol %) | | | | | | MeOH conversn (%) | CO selectivity [yield][c] (%) | H₂ selectivity [yield][c] (%) | balance | |
		MeOH	MF[a]	H₂	CO	CO₂	DME[b]				H/4C	O/C
225	Cu/Cr/Mn	39.95	9.13	40.05	10.49	0.14	0.24	42.4	35.7 [15.1]	67.8 [28.7]	1.01	1.00
	Cu/Cr/Mn/Na (2%)	35.72	7.55	43.34	13.16	0.15	0.07	44.4	46.1 [20.5]	73.9 [32.8]	1.02	1.00
	Cu/Cr/Mn/K (2%)	35.28	6.02	43.84	14.64	0.15	0.07	43.3	54.3 [23.5]	78.1 [33.8]	1.03	1.00
250	Cu/Cr/Mn	30.15	6.27	46.71	16.36	0.25	0.26	49.6	55.1 [27.3]	78.8 [39.1]	1.01	1.00
	Cu/Cr/Mn/Na (2%)	26.93	5.89	48.29	18.37	0.29	0.23	53.4	59.5 [31.8]	79.5 [42.6]	0.99	1.00
	Cu/Cr/Mn/K (2%)	25.21	3.68	50.09	20.59	0.31	0.12	53.1	72.3 [38.4]	86.7 [46.0]	1.01	1.00
275	Cu/Cr/Mn	21.71	4.84	51.30	21.17	0.47	0.51	59.8	66.5 [39.8]	82.1 [49.1]	0.97	1.00
	Cu/Cr/Mn/Na (2%)	18.88	3.95	53.65	22.79	0.47	0.26	62.7	71.9 [45.1]	86.1 [54.0]	0.99	1.00
	Cu/Cr/Mn/K (2%)	17.14	2.32	55.80	24.03	0.48	0.15	63.2	81.6 [51.6]	91.6 [57.9]	1.03	1.01

[a] MF = methyl formate. [b] DME = dimethyl ether. [c] Yield = conversion of methanol × selectivity.

Table 2. Effect of Potassium Additive on Some Properties of Freshly Reduced G89 Catalyst and Its CO Yield in Methanol Decomposition at 250 °C, 1 atm, and 10 000 L (STP)/h/kg of catalyst of Gas Hourly Space Velocity

catalyst	Cu crystallite size (nm)	Cu surface area (m²/g of Cu)	initial CO yield (%)
Cu/Cu/Mn	12.5	31.5	32.5
Cu/Cr/Mn/K (1%)	11.8	35.6	38.1
Cu/Cr/Mn/K (2%)	11.2	38.9	42.0
Cu/Cr/Mn/K (4%)	10.4	40.7	46.5

Table 3. Effect of CO₂ on Deactivation of a Cu/Cr/Ba/Si (85/10/2.5/2.5) Catalyst in Methanol Decomposition at 275 °C

feed	deactivation rate constant (1/h)
100% MeOH	2.2×10^{-3}
87/13 MeOH/CO₂	9.8×10^{-4}
77/23 MeOH/CO₂	2.5×10^{-4}

copper, morphology, and phase distribution were also investigated. However, no consistent correlation was found.

Catalyst Stability. Studies have shown that although Cu/Cr-based catalysts are much more stable than Cu/Zn-based catalysts in methanol decomposition, they still gradually deactivate.[7] A regeneration method was developed which can completely and repeatedly restore the catalyst activity.[7,34] The deactivated catalyst was first oxidized in air at 300−450 °C followed by reduction in a H₂-containing atmosphere at 200−300 °C. The regeneration can be conducted in situ in the reactor. In addition to the approach of developing an effective regeneration method, an alternative and preferred approach is to develop more stable catalysts or reaction processes, if they can be achieved and effectively conducted.

It is interesting to note that cofeeding CO₂ with methanol significantly retards the deactivation of a Cu/Cr-based catalyst used in methanol decomposition.[35] The deactivation can fit with second-order deactivation kinetics. The deactivation rate constant decreased by about 2.3 times when 13 mol % CO₂ was added in the methanol feed and by an order of magnitude when 23% CO₂ was added in the feed (Table 3).[35] The deactivation rate decreased with the CO₂ concentration in the methanol/CO₂ feed either at constant total pressure or at constant methanol partial pressure.

The product distribution over the Cu/Cr-based catalyst with and without cofeeding CO₂ shows that CO₂ does not change the initial conversion and selectivity of the metha-

Table 4. Properties of a Cu/Cr/Mn Catalyst (G89) before and after Methanol Decomposition and after Regeneration

catalyst	Cu crystallite size (nm)	Cu surface area (m²/g of Cu)	C content (wt%)
freshly reduced	12.3	31.5	1.91
used (MeOH/CO₂ 90/10)	13.0	28.1	3.31
used (MeOH/N₂)	14.2	20.4	3.94
regenerated		30.8	2.03

nol decomposition reaction. The enhancement of the catalyst stability by CO₂ was also observed for other Cu/Cr-based catalysts such as Cu/Cr/Zn and Cu/Cr/Ba. The role of CO₂ in enhancing the stability will be elucidated later with the causes of catalyst deactivation. If the fresh CO₂ is not readily available such as in the case of on-board vehicle application, CO₂ may be obtained by making use of the CO₂-rich exhaust gas from engines.

Causes of Catalyst Deactivation. The causes of deactivation of Cu-based catalysts in methanol decomposition or in dehydrogenation to methyl formate have been controversial. Three possibilities may exist if the feed does not contain poisonous impurities.

First, Cu sintering has been proposed to be a reason for the deactivation in methanol decomposition and dehydrogenation.[35,36] The melting point of Cu is relatively low, and Cu-based catalysts are generally vulnerable to deactivation by thermal sintering. Second, it was shown that carbon deposition contributed to the deactivation in methanol decomposition[7] and dehydrogenation.[37] The polymerization of formaldehyde which was formed via eq 3 could lead to coke formation.[38] Thermodynamically, the disproportionation reaction ($2CO \rightleftharpoons CO_2 + C_{(s)}$) is strongly favored in the forward direction under typical methanol decomposition conditions. Limiting H₂ to CO ratios at various temperatures and pressures have been calculated below which carbon deposition may occur.[39] The H₂ to CO ratio in a typical methanol decomposition reactor is below the limiting ratio. Therefore, carbon deposition could occur. However, the kinetic observation in this area has been lacking. Third, the change of catalyst structure such as catalyst phases and oxidation state of Cu, if it occurred, could also change the catalyst activity.

Table 4 shows some properties of a Cu/Cr/Mn (NGC G89) catalyst before the reaction, after the reaction, and after the regeneration.[35] The used catalysts were obtained after 96 h of methanol decomposition reaction in methanol/CO₂ or in methanol/N₂ at 275 °C. The Cu crystallite size increased and the Cu surface area decreased when

the catalyst deactivated. The degree of Cu sintering was suppressed when the methanol feed contained CO_2. The carbon content increased significantly after the reaction. The degree of carbon deposition was also suppressed when the methanol feed contained CO_2. The redispersion of Cu species occurred, and the carbon content was also restored to that of the fresh catalyst after the regeneration. These results consistently indicate that Cu sintering and carbon deposition contribute to the catalyst deactivation at high reaction temperatures. Both Cu sintering and carbon deposition can be significantly suppressed by CO_2, and this is consistent with the enhancement of catalyst stability by CO_2. On the other hand, no consistent correlation was found between catalyst deactivation and a change of catalyst phases or oxidation state of Cu.

Role of the Components. On the basis of the above results, highly active Cu-based low-temperature methanol decomposition catalysts may contain Cu and elements selected from Cr, Mn, Ba, Si, and K. ZnO is an undesired and unnecessary component in methanol decomposition in the absence of water. The role of each component is briefly discussed below.

(1) Cu: It was shown that Cu species, probably metallic Cu, is the active species for methanol decomposition.[8] Whether Cu^0 or Cu^+ is the active species in the methanol synthesis reaction has been controversial for over a decade.[40−43] The same controversy also occurred for methanol decomposition. Two important things which have often been overlooked need to be considered in determining and discussing active species. (1) Both Cu^0 and Cu^+ species may be active but differ in their selectivities and active temperature range. For example, in a recent study on methanol decomposition over copper/aluminum oxide catalysts,[44] it was shown that metallic copper catalyzed the dehydrogenation of methanol to methyl formate at 210 °C or lower. Metallic copper decomposed methyl formate to CO and methanol at above 210 °C. $CuAlO_2$ was active for the selective methyl formate formation but was inactive above 330 °C. $CuAl_2O_4$ decomposed methanol above 330 °C. (2) Metallic Cu in some Cu-based catalysts can be oxidized even at room temperature in a short period. A freshly activated Cu/Cr/Mn catalyst (NGC G89) which was prereduced in situ in 10% H_2 in N_2 at 250 °C for 3 h showed no further reduction (TPR) by H_2 or CO up to about 600 °C.[35] Possible oxidized Cu species such as CuO, Cu_2O, $CuCr_2O_4$, or $CuCrO_2$ if present would have been detected well below 600 °C in the TPR study. Cu in the reduced catalyst was in the metallic state. However, exposing the activated catalyst in flowing air at room temperature for 5 min caused the oxidation of Cu to Cu_2O, which was clearly indicated by a H_2 consumption peak at about 160 °C in the subsequent TPR study. The result was in agreement with an in situ XRD study which indicated that only a crystalline metallic Cu phase in a Cu/Cr/Mn catalyst was found during in situ reduction.[8] The Cu_2O phase was formed after exposing the catalyst to air at room temperature. In situ investigation or careful handling of treated-Cu based catalysts avoiding air exposure is necessary to elucidate the effect of the Cu oxidation

state. A TPR study on a used G89 catalyst with minimal exposure to air showed little oxidized Cu peaks.[35] These results strongly suggest that Cu is almost present in the metallic Cu state in a methanol decomposition reactor, a reducing enviromnent, and the metallic Cu is active for methanol decomposition. However, this does not exclude Cu^+ from being an active species. To further investigate whether Cu^+ is also active, a nonreduced Cu-based catalyst was used in the methanol re-forming reaction.[45] The reactivities were conducted over the catalyst at the initial transient period of the reaction at 250 °C. The TPR study was also conducted on used catalysts taken at various times on the stream. The oxidation state of Cu gradually decreased with time on the stream. The correlation between the Cu oxidation state and catalyst activity suggests that Cu^+ is more active than Cu^0 in methanol re-forming and Cu^{2+} is least active.

(2) Zn: Although ZnO is a necessary component in Cu-based catalysts in the methanol synthesis reaction, it is an undesired component in methanol decomposition. Although ZnO may help to disperse or support active Cu species, the activity of Cu/ZnO-containing catalysts quickly decreases in methanol decomposition (Figure 3). It was suggested that ZnO was reduced in the initial reaction of methanol decomposition. This reduction facilitated the dissolution of Zn into the Cu lattice, forming *a*-brass (Figure 4). The Zn content in *a*-brass increased with reaction temperature. The surface content of zinc would be much higher than that in the bulk because of the surface segregation of zinc.[46]

(3) Cr: CuO and $CuCr_2O_4$ phases were found in calcined Cu/Cr-based catalysts such as NGC G89 (Cn/Cr/ Mn) catalyst.[29] The reduced catalysts showed only the crystalline Cu phase. No oxidized Cu-containing or crystalline Cr or Mn phases were found by XRD in the reduced catalysts. $CuCr_2O_4$ can be reduced to Cu and Cr_2O_3 via $Cu_2Cr_2O_4$ intermediate.[47,48] CuO and Cu_2O in Cu/Cr-based catalysts can be readily reduced to Cu in hydrogen at temperatures below 250 °C.[8,48] Cr in the form of chromium oxide can stabilize the dispersion of the active Cu and is an essential component to achieve good stability.[8] However, the acidic nature of chromium oxide causes a small loss of the CO selectivity due to its dehydration activity to form dimethyl ether.

(4) Si, Ba, or Mn: A small amount of Si, Ba, or Mn (typically, 2−4 wt %) increased the catalyst activity. Silica in the form of amorphous silica may act as a textural promoter, which increases the dispersion of Cu.[8] The promoting mechanism of barium or manganese oxides in methanol decomposition has not been clear. It was suggested that BaO may inhibit the complete reduction of divalent Cu.[49] However, the effect of barium and manganese oxides on Cu valence in methanol decomposition and the correlation of this effect with catalyst performance have not been clearly established.

(5) Alkali elements: Addition of alkali elements on Cu/ Cr-based catalysts was shown to substantially decrease the formation of dimethyl ether (Table 1). It was believed that alkali elements passivated the acidic nature of chromium

oxide and decreased the activity of the dehydration reaction of methanol. Alkali metal additives also enhanced the activity of methanol decomposition. This was partially attributed to the increased dispersion of Cu revealed by both the Cu surface area and Cu crystallite size measurements (Table 2). When the specific free energy of formation of a metal film on a substrate is greater than zero, as in the cases of most metals on oxides, the metal does not wet the substrate well.[50] To decrease the free energy of the system, the metal particle will tend to coalesce. Addition of alkali elements such as potassium in Cu-based catalysts was shown to interact with Cu and form a Cu/K interface.[51] The interaction would reduce the free energy of the system and help to stabilize Cu spreading. The interface between Cu and K provided an adsorption site for methyl formate,[51] an intermediate in methanol decomposition, and could also contribute to the enhancement of the activity.

Conclusions

Cu/Cr-based catalysts are much more active than the conventional Cu/Zn catalysts in methanol decomposition. The acidic nature of the Cu/Cr-based catalysts, which leads to the decreased selectivity, can be greatly reduced by passivating the catalysts with alkali metal ions such as potassium.

A series of promoters to further enhance catalyst activity were found for Cu-based methanol decomposition catalysts. These promoters include SiO_2, alkali metal ions, and oxides of Mn and Ba. The increased dispersion of Cu was evidenced when a small amount of SiO_2 or alkali metal was added.

It was also found that cofeeding CO_2 with methanol can significantly enhance the stability of Cu-based catalysts by retarding both Cu sintering and carbon deposition. Unlike oxygen and water, which are often reactive to induce oxidation or the re-forming reaction, CO_2 is relatively unreactive to change the product distribution at mild reaction temperatures but can enhance the catalyst stability. The result suggested a new role of CO_2 and a new way to increase the stability of heterogeneous catalysts.

Some promising applications of methanol decomposition such as gas turbine fuel and on-site source of CO and H_2 may need the reaction conducted at elevated pressure. Extension of the study of the methanol decomposition catalysts to elevated pressure will be needed to commercialize the catalyst and reaction process.

References

(1) Winter, C. J. Hytime-It Is High Time for Hydrogen. *Proceedings of the 11th World Hydrogen Energy Conference*, Stuttgart, Germany, June 1996; pp 3−12.

(2) Amphlett, J. C.; Mann, R. F.; Peppley, B. Performance and Operating Characteristics of Methanol Steam-reforming Catalysts for On-board Fuel-cell Hydrogen Production. *Proceedings of the 11th World Hydrogen Energy Conference*, Stuttgart, Germany, June 1996; pp 1737−1744.

(3) Yoon, H.; Stouffer, M. R.; Dubt, P. J.; Burke, F. P.; Curran, G. P. Methanol Dissociation for Fuel Use. *Energy Prog.* **1985**, 5, 78−83.

(4) Cheng, W. H.; Kung, H. H. Overview. In *Methanol Production and Use*; Cheng, W. H., Kung, H. H., Eds.; Marcel Dekker: New York, 1994; Chapter 1.

(5) Pettersson, L.; Sjostrom, K. Decomposed Methanol as a Fuel-a Review. *Combust. Sci. Technol.* **1991**, 80, 265−303 and references therein.

(6) Cheng, W. H. Development of Methanol Dissociation Technology. 9th ROC-Japan Catalysis Symposium, Nanton, Taiwan, February 1998.

(7) Cheng, W. H. Deactivation and regeneration of methanol Decomposition Catalysts. *Appl. Catal. B: Environ.* **1995**, 7, 127−136.

(8) Cheng, W. H. Reaction and XRD Studies on Cu Based Methanol Decomposition Catalysts: Role of Constituents and Development of High-activity Multicomponent Catalysts. *Appl. Catal. A: Gen.* **1995**, 130, 13−30.

(9) Karpuk, M. E. *Design and Testing of a Dissociated Methanol Vehicle*; DOE/CH/10039-H5; U.S. Department of Energy: Washington, DC, 1989.

(10) Sakai, T.; Yamaguchi, I.; Asano, M.; Ayusawa, T.; Kim. Y. K. *Transient Performance Development on Dissociated Methanol Fueled Passenger Car*; SAE paper 871169; 1987.

(11) Woodley, N. H.; Nordman, D.; Legro, J. R.; Davies, D. G. *Reformed Alcohol Fuels for Combustor Turbines: Technical and Economical Feasibility Assessment*; Report No. SERI/TR 11290-1; Solar Energy Research Institute: Golden, CO, 1982.

(12) Tsuruno, S.; Kaneko, Y.; Fujimoto, S. Gas Turbine Cycle with Decomposing Methanol. *Proceedings of the VI International Symposium on Alcohol Fuels, Technology*, Ottawa, Canada, May 1984; p 385.

(13) Baba, S. Research and Development of Reformed Methanol Gas-type Power Generation System. *Proceedings of the VIII International Symposium on Alcohol Fuels*, Tokyo, November 1988; p 945.

(14) Okano, K. R&D of Hydrogen Utilization Technologies: WE-NET Program and Fuel Cell Activities in Japan. *Proceedings of the 11th World Hydrogen Energy Conference*, Stuttgart, Germay, June 1996; pp 1667−1673.

(15) Exhibits presented at the 11th World Hydrogen Energy Conference, Stuggart, Germany, June 1996.

(16) Jost, K. Gasoline-Reforming Fuel Cell. *Automot. Eng.* **1997** (Feb), 151−152.

(17) Kostelitz, V. O.; Huttig, G. F. Das System Zinkoxid/Kupferoxid als Katalysator des Methanolzerfalles. *Kolloid Z.* **1934**, 67, 265−277.

(18) Frolich, P. K.; Fenske, M. R.; Quggle, D. Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen I-Decomposition of Methanol by Catalysts Composed of Copper and Zinc. *Ind. Eng. Chem.* **1928**, 20, 694−698.

(19) Cheng, W. H. Controlled-environment XRD Study Cu/ZnO Related to Activity in Methanol Decomposition. *Mater. Chem. Phys.* **1995**, 41, 36−40.

(20) Smith, K. J.; Anderson, R. B. A Chain Growth Scheme for the Higher Alcohols Synthesis. *J. Catal.* **1984**, 85, 428−436.

(21) Aas, N.; Pringle T. J.; Bowker, M. Adsorption and Decomposition of Methanol on TiO_2, $SrTiO_3$ and SrO. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1015−1022.

(22) Cheng, W. H.; Akhter S.; Kung, H. H. Structure Sensitivity in Methanol Decomposition on ZnO Single-Crystal Surfaces. *J. Catal.* **1983**, *82*, 341−350.

(23) Akhter, S.; Cheng, W. H.; Kung, H. H. Decomposition of Methanol, Formaldehyde, and Formic Acid on Nonpolar(10$\bar{1}$0), Stepped(50$\bar{5}$1), and Polar(0001) Surface of ZnO by Temperature-progrommed Decomposition. *J. Catal.* **1984**, *85*, 437−456.

(24) Edwards, J. F.; Schrader, G. L. Methanol, Formaldehyde and Formic Acid Adsorption on Methanol Synthesis Catalysts. *J. Phys. Chem.* **1985**, *89*, 782−788.

(25) Chadwick, D.; Zheng, K. The Importance of Water in the Mechanism of Methanol Decomposition. *Catal. Lett.* **1993**, *20*, 231−242.

(26) Shlegel, L.; Gutshik, D.; Rozovskii, A. Decomposition of Methanol on Methanol Synthesis Catalysts Containing Copper. *Kinet. Katal.* **1990**, *31*, 880−882.

(27) Schmitz, A. D.; Eyman, D. P.; Gloer, K. B. Highly Active Methanol Decomposition Catalysts Derived from Supported Molten Salts. *Energy Fuels* **1994**, *8*, 729−740.

(28) Cheng, W. H.; Ferretti, A. Methanol Dissociation Catalysts. U.S. Patent 5,106,810, 1992.

(29) Cheng, W. H.; Shiau, C. Y.; Liu, T. H.; Tung, H. L.; Lu, J. F.; Hsu, C. C. Promotion of Cu/Cr/Mn Catalysts by Alkali Additives in Methanol Decomposition. *Appl. Catal. A: Gen.* **1998**, *170*, 215−224.

(30) Cosimo, J. I. D.; Apesteguia, C. R. Use of the Methanol Decomposition Reaction for Identifying Surface Species in Cu/Co-based Catalysts. *J. Mol. Catal.* **1994**, *91*, 369−386.

(31) Nunan, J. G.; Herman, R. G.; Klier, K. Higher Alcohol and Oxygenate Synthesis over $Cs/Cu/ZnO/M_2O_3$-(M=Al, Cr) Catalysts. *J. Catal.* **1989**, *166*, 222−229.

(32) Evans, J. W.; Wainwright, M. S.; Bridgewater, A. J.; Young, D. J. On the Determination of Copper Surface Area by Reaction with Nitrous Oxide. *Appl. Catal.* **1983**, *7*, 75−83.

(33) Grift, V. D.; Wielers, A. F.; Joghi B. P.; Beijnum, J. V. Effect of the Reduction Treatment on the Structure and Reactivity of Silica-supported Copper Particles. *J. Catal.* **1991**, *131*, 178−189.

(34) Cheng, W. H. Calcination on CO_2 of Methanol Dissociation Catalysts. U.S. Patent 4,826,798, 1989.

(35) Cheng, W. H.; Shiau, C. Y.; Liu, T. H.; Tung, H. L.; Chen, H. H.; Lu, J. F.; Hsu, C. C. Stability of Copper Based Catalysts Enhanced by CO_2 in Methanol Decomposition. *Appl. Catal. B: Environ.* **1998**, *13*, 63−70.

(36) Sodesawa, T.; Nagacho, M.; Onodera A.; Nozaki, F. Dehydrogenation of Methanol to Methyl Formate Over Cu−SiO_2 Catalysts Prepared by Ion Exchange Method. *J. Catal.* **1986**, *102*, 460−463.

(37) Ovesen, C. V.; Clausen, B. S.; Schiotz, J.; Stoltze, P.; Topsoe, H.; Norskov, J. K. Kinetic Implications of Dynamical Changes in Catalysts Morphology During Methanol Synthesis Over Cu/ZnO Catalysts. *J. Catal.* **1997**, *168*, 133−142.

(38) Miyazaki, E.; Yasumori, I. Kinetics of the Catalytic Decomposition of Methanol, Formaldehyde and Methyl Formate over a Copper-Wire Surface. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2012−2017.

(39) Mills, G. A.; Steffgen, F. W. Catalytic Methanation. *Catal. Rev.* **1973**, *8*, 159−200.

(40) Sheffer, G. R.; King, T. S. Potassium's Promotional Effect of Unsupported Copper Catalysts for Methanol Synthesis. *J. Catal.* **1989**, *115*, 376−387.

(41) Yoshihara, J,; Parker, S. C.; Schafer, A.; Campbell, C. T. Methanol Synthesis and Reverse Water-Gas Shift Kinetics over Clean Polycrystalline Copper. *Catal Lett.* **1995**, *31*, 313−324.

(42) Sizgek, G. D.; Curry-Hyde, H. E.; Wainwright, M. S. Methanol Synthesis over Copper and ZnO Promoted Copper Surfaces. *Appl. Catal. A* **1994**, *115*, 15−28 and references therein.

(43) Klier, K. Methanol Synthesis. *Adv. Catal.* **1982**, *31*, 243−313 and references therein.

(44) Sato, S.; Iijima, M.; Nakayama, T.; Sodesawa, T.; Nozaki, F. Vapor-Phase Dehydrocoupling of Methanol to Methyl Formate Over $CuAl_2O_4$. *J. Catal.* **1997**, *169*, 447−454.

(45) Cheng, W. H.; Chen, I.; Jany, Y. C. Steam Reforming of Methanol Over Cu/Cr/Mn Catalysts. To be submitted.

(46) Spencer, M. S. *a*-bass Formation in Copper/Zinc Oxide Catalysts. *Surf. Sci.* **1987**, *192*, 323−328.

(47) Tu, Y. J.; Chen, Y. W.; Li, C. Characterization of Unsupported Copper−Chromium Catalysts for Ethanol Dehydrogenation. *J. Mol. Catal.* **1994**, *89*, 179−190.

(48) Tonner, S. P.; Wainwright, M. S.; Trimm, D. L.; Cant, W. W. Characterization of Copper Chromite Catalysts for Methanol Dehydrogenation. *Appl. Catal.* **1984**, *11*, 93−101.

(49) Adkins, H.; Burgoyne, E.; Schneider, H. The Copper-Chromium Oxide for Hydrogenation. *J. Am. Chem. Soc.* **1950**, *72*, 2626−2629.

(50) Ruckenstein, E. Wetting and Spreading. In *Metal-Support Interaction, in Catalysis, Sintering, and Redispersion*; Stevenson, S. A., Dumesic, J. A., Baker, R. T. K., Ruckenstein, E., Eds.; Van Nostrand Reinhold: New York, 1987; Chapter 13.

(51) Millar, G. J.; Rochester, C. H.; Waugh, K. C. An FTIR Study of the Adsorption of Methanol and Methyl Formate on Potassium-Promoted Cu/SiO_2 Catalysts. *J. Catal.* **1993**, *142*, 263−273.