DEACTIVATION OF METHANOL SYNTHESIS CATALYSTS - A REVIEW

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ABSTRACT

The current knowledge of the deactivation phenomenon of the low-temperature gas-phase methanol synthesis catalyst is reviewed. Under normal operating conditions, the catalyst Cu-Zn oxide has a rather long lifetime of a few years. However, the catalyst is very sensitive to sulfur poisoning, and the sulfur content in the feed stream needs to be reduced to less than 0.5 ppm. The ZnO component in the catalyst is a scavenger for sulfur by reacting with it to form Zn sulfide and sulfate, which helps extend the catalyst life. The catalyst can also be deactivated thermally, especially at above 300 °C because of the growth of the Cu crystallites and the resulting loss of catalytically active area. Deposition of Fe or Ni results in loss of activity by site blocking as well as production of hydrocarbon products as a competitive reaction, whereas Cl facilitates sintering of Cu. The catalyst for the liquid-phase synthesis is also susceptible to the same types of deactivation. Catalysts derived from Cu-rare earth alloys are very susceptible to deactivation by CO_2, O_2, and to a lesser extent, H_2O.

INTRODUCTION

The production of methanol has been a large-scale industrial process for many years. At present, over 75% of the world's production makes use of the ICI low-pressure process (ref. 1). The process operates at 220 to 300 °C and 5 to 8 MPa pressure and uses a series of catalytic adiabatic reactor beds with interbed cooling by injection of cold synthesis gas. The catalyst is typically $Cu/Zn/Al_2O_3$ or, less preferably, $Cu/Zn/Cr_2O_3$, which contains 50 to 70 wt % CuO and 20 to 30 wt % ZnO. The feed is synthesis gas that may be produced by catalytic reforming of natural gas, other hydrocarbons, or coal and contains a mixture of carbon monoxide, carbon dioxide, and hydrogen in a ratio of 10-20:6-10:70-80. Because of the industrial importance of this process, a number of reviews have appeared that describe in detail the nature of the catalyst, the kinetics, and the reaction mechanism (refs. 1-4).

In the typical plant operation, the catalyst lifetime is about 2 years, and the reactor temperature is slowly varied to compensate for the loss in catalytic activity (refs. 1-5). A major cause for catalyst deactivation is known to be sulfur poisoning. Typically, the sulfur

concentration in the feed must be reduced to 0.5 ppm, preferably 0.1 ppm (ref. 6). A higher sulfur concentration would cause noticeably faster deactivation (ref. 7). Other causes for deactivation have also been identified. These include sintering of crystallites of Cu or CuO, decrease in pore volume, and deposition of other metals. Surprisingly, in spite of the importance of deactivation to plant operation, relatively few studies have been reported on the phenomenon, and only one of the recent reviews has devoted a section to it (ref. 1). This paper is a review of the recent literature on the deactivation of the methanol synthesis catalyst. The emphasis of the paper is on the current industrial catalyst of Cu-Zn oxide, but a brief discussion of the laboratory catalyst of Cu intermetallics is also included.

METHANOL SYNTHESIS OVER Cu-Zn OXIDE CATALYSTS

The industrial methanol synthesis process is a gas phase process. A liquid phase process has been under development for some time. Both processes use essentially the same catalyst, therefore, they share some common deactivation phenomena.

Gas Phase Process
Nature of the catalyst

The catalyst can be prepared by precipitation from a mixture of copper, zinc, and aluminum nitrate using a carbonate. X-ray diffraction of the precipitates showed a mixture of $Cu_2(OH)_3NO_3$ and $(Cu,Zn)_2(OH)_2CO_3$, $Zn_5(OH)_6(CO_3)_2$, which might contain some Cu, and $12Al(OH)_3.Al_2(CO_3)_3$ (refs. 1, 8, 9). Upon calcination, $(Cu,Zn)_2(OH)_2CO_3$ decomposes into a very fine dispersion of zinc oxide and copper oxide. Subsequent reduction results in a catalyst containing metallic copper crystallites and ZnO particles (ref. 9, 10). There may also be substitutional Cu(I) ions in some ZnO particles.

There have been two proposals on the nature of the active site. The presence of substitutional Cu(I) ions has led to the proposal that they are the active sites (ref.9), but this has not been supported by direct experimental evidence. On the other hand, results of x-ray photoelectron spectroscopic analysis of the catalysts (ref. 11) and a successful correlation of the catalytic activities with the metallic Cu surface area as determined by N_2O decomposition activity (refs. 1, 12) suggest that metallic Cu is the active site. The high activity of the catalyst is then attributed to the ability of ZnO to stabilize finely dispersed Cu crystallites, which provide a high surface area of the active component. There is also the possibility of electronic effects resulting from the small size of the crystallites and their interaction with the support.

Reaction mechanism

Because both CO and CO_2 are present in the reaction mixture and they interconvert rapidly via the water-gas shift (WGS) reaction (CO + H_2O = CO_2 + H_2), there has been much discussion of the proximate source of carbon for methanol. Critical discussion of the available literature data can be found in references 2 and 3. It appears that there is strong evidence based on isotope labeling studies that CO_2, and not CO, is the proximate carbon source (refs. 1, 13-15). The reaction proceeds by hydrogenation of CO_2 to a surface formate, which is further hydrogenated eventually to methanol. Whether a surface formyl species is also formed is not firmly established.

Because CO_2 is the proximate source of carbon, it is necessary that a good methanol synthesis catalyst to be a good (WGS) catalyst also. This will ensure process flexibility to accommodate a wide range of CO/CO_2 ratios in the feed stream and eliminate the need to separately CO into CO_2 separately. Indeed, a commercial low-temperature shift catalyst contains the same components as a methanol synthesis catalyst, and copper is the active phase (ref.16).

Initial deactivation

In laboratory tests using microreactors, a fresh catalyst that has been calcined is first activated by reduction, often with hydrogen. The resulting catalyst is black in color. The methanol synthesis activity of a reduced catalyst is initially high and declines in the next few hours by as much as 60% (refs. 17, 18). Depending on the amount of catalyst and the reaction conditions, the catalyst takes from 1 to 20 h to reach steady state. Other than the decline in activity, however, there are no detectable changes in the other properties of the catalyst: the phase composition, the crystallite morphology, the surface chemical composition (ref. 8), or the dependence of the activity on the CO/CO_2 ratio in the feed (ref. 17). Thus, this initial rapid deactivation is probably due to loss of surface area when some of the very finely dispersed Cu crystallites agglomerate. The slow approach to steady state of the surface coverages of some reaction products and intermediates, especially water, may also contribute to this transient. It has been shown that high partial pressures of water inhibit the reaction, presumably by competitive adsorption on the active sites (as indicated by the negative order in water partial pressure (refs. 1-4)), and the fact that recovery of the activity by removal of water occurs only slowly (refs. 18, 19).

Deactivation by sulfur poisoning

Sulfur is the most common poison because it is present in the source materials for synthesis gas. The Cu-Zn oxide catalyst is very susceptible to sulfur poisoning. As mentioned earlier, a few ppm of sulfur in the feed would cause noticeable reduction in activity. Wood et al. studied the kinetics of poisoning by sulfur present as H_2S, thiophene, and COS under conditions in which there was no external mass-transfer limitation (ref. 7). For an inlet concentration of H_2S from 1.6 to 33 ppm, the catalytic activity decays exponentially so that the time change in the rate of methanol production follows the equation:

$$d \ Rate_{MeOH}/dt = -kC_{HS} \tag{1}$$

where k is the poisoning constant whose value at 503 K is 0.8×10^{-4} L/mol-h, and C_{HS} is the concentration of H_2S in mol-$L^{-1} \times 10^6$. The effect of H_2S deviates from this first order equation at concentrations higher than 40 ppm, presumably due to mass-transfer complication of intraparticle diffusion of H_2S.

A comparison of the rates of deactivation by H_2S , thiophene, and COS is shown in Table 1. The rate of deactivation by thiophene is slightly faster than by H_2S. It also follows the same first-order dependence on the concentration of thiophene. The poisoning constant at 503 K is 1.0×10^{-4} L/mol-h for a thiophene concentration of 3 to 5.4 ppm. Unlike thiophene or H_2S, COS does not cause any deactivation at all over a concentration range of 0.6 to 9 ppm. There is no decomposition of COS or reaction of COS with H_2 to form H_2S over the catalyst at 503 K.

Surface analyses by Auger spectroscopy of catalysts deactivated by H_2S have shown that at low exposures to H_2S the adsorbed sulfur suppresses the Cu signal more significantly than the Zn signal, which suggests that decomposition of H_2S to adsorbed sulfur takes place more efficiently on Cu than on ZnO (ref. 7). Interestingly, the results also show that there is much less sulfur deposited on the catalyst by thiophene than by H_2S, although the former is a more effective poison (Table 1). This suggests that thiophene decomposes on the copper surface and deposits sulfur at the active site more selectively than H_2S. After a high exposure to H_2S, ZnS is formed as a separate phase in the catalyst at the expense of ZnO, but no copper sulfide phases have been detected, consistent with the fact that at H_2S concentrations below 30 ppm, neither Cu_2S nor CuS is thermodynamically stable.

Results reported in a recent publication are in general agreement with the observations mentioned above (ref. 20). X-ray diffraction (XRD) analyses of a catalyst deactivated by pulsing H_2S in a laboratory have shown that sulfur is present principally as

TABLE 1

Effectiveness of poisoning by different sulfur-containing compounds[a].

S compound	Conc. ppm	Deact. rate	Total exposure 10^{-3} mol/g.cat	S content on surface
H_2S	3.2	50% in 26 h	0.09	22%
thiophene	5	50% in 13 h	0.11	3%
COS	0.6-9	none	-	-

[a]Cu-Zn oxide catalyst, 503 K, $CO/H_2/CO_2$ = 33/65/2 (ref. 7).

TABLE 2

Effect of Cu/Zn ratio on the deactivation by sulfur[a].

Cu/Zn/Al	No. H_2S pulses	Wt% S^b	Deact. rate^c (%)
4/4/1	13	10.52	58.9
4/5/1	13	~10	68.1
8/4/1	12	~9	62.2
4/8/1	12	9.14	73.6

[a] 523 K, 5 MPa, 14 to 16% CO, 67% H_2, the balance presumably was CO_2 (ef. 20).
[b] Amount on the catalyst after H_2S pulses.
[c] Percent of initial activity (i.e., before H_2S pulses).

ZnS. Interestingly, a catalyst deactivated in an industrial reactor showed also $Zn_3O(SO_4)_2$ and $Cu_{1.5}ZnSO_4(OH)_3$. These sulfates can be extracted with water. The formation of sulfate could be due to the much higher conversion in a commercial reactor such that the gas phase is less reducing, particularly near the outlet of the reactor.

Because sulfur is primarily associated with Zn, it has been suggested that an important function of ZnO in the catalyst is to scavenge sulfur, and catalysts of higher ZnO contents are more resistant to sulfur poisoning. This is illustrated by the data in Table 2 (ref. 20).

Catalysts of the same exposure to H_2S contain about the same amounts of sulfur deposits, but those with a higher Zn content show less deactivation. The commercial catalyst can maintain 80% of its activity containing 2 wt% sulfur, and 25% to 50% of its activity containing 10% to 12% sulfur (refs. 1, 20).

The effects of sulfur on the methanol production activity apply equally well to the WGS activity of the catalyst. For a low-temperature shift catalyst that contains the same components of copper, zinc, and aluminum oxides, it has been reported that the loss of activity of a catalyst is less than a few percent after 15 months of operation in a laboratory apparatus free of sulfur (and chlorine) while the catalyst in a commercial unit has lost at least 25% of its activity (ref. 16). Such catalysts can absorb 0.4 wt% sulfur while maintaining over 70% of their shift activities. XRD results show that most of the sulfur forms ZnS.

There is no information on the mechanism of sulfur poisoning. If the active sites are metallic Cu surfaces, sulfur probably poisons by physical blocking of the surface. Under the normal operating condition, neither CuS nor Cu_2S is stable. If the active sites are surface interstitial Cu(I) ions, sulfur poisoning could be a result of the following reaction (ref. 8):

$$Cu^I + O^{2-} + H_2S = Cu^ISH^- + OH^- \qquad (2)$$
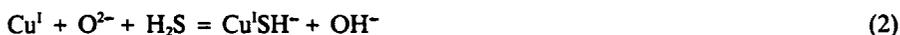
The high sensitivity of the catalyst to sulfur poisoning leads to the logical question of whether or not a more sulfur resistant but equally active and selective catalyst should be developed. The economic analysis of Dalla Betta and Ushiba suggests that, if the synthesis gas is derived from a high sulfur coal, there is only marginal economic incentive to develop a sulfur-resistant catalyst, because the cost of bulk desulfurization far exceeds the incremental cost to reduce sulfur to a trace level (ref. 6). However, such a catalyst would provide greater process reliability and flexibility.

Deactivation by chlorine

Unlike sulfur, chlorine is not normally present in the feed stream except when it is contaminated, e.g., by unpurified water. It has been reported for the WGS catalyst that the Cu crystallite size increases drastically on catalysts poisoned by chlorine to the extent that the catalyst takes on a coppery color (ref. 16). The much enhanced rate of sintering of copper crystallites is probably due to the formation of volatile copper chloride compounds. This deactivation mechanism would apply to a methanol synthesis catalyst if it occurs.

Deactivation by metal deposition

Trace amounts of metal carbonyl compounds could be present in the feed streams, especially in laboratory experiments where stainless steel is used to construct the reactor and for tubings for gas handling. The metal that is deposited onto the catalyst when the volatile carbonyl decomposes would block the active sites as well as provide unwanted catalytic activities. For example, deposition of iron could occur with iron carbonyl that is formed from the stainless steel tubing used, and the catalyst could become nonselective for methanol production. The formation of hydrocarbons by the Fischer-Tropsch reaction catalyzed by iron becomes a competing reaction. This might be the explanation for the observations of Denise et al. who found that the amounts of methane and other hydrocarbons increased with time of reaction and the methanol selectivity decreased (ref. 21). It might also contribute to the lack of attainment of steady-state activity in the study by Radovic and Vannice (ref. 22). Likewise, Ni deposited from $Ni(CO)_4$ would lower the catalyst selectivity by enhancing the production of methane.

Another potential source of metal are the impurities present in the precursor materials used to prepare the catalyst. It is known that a Cu-Zn oxide catalyst containing a few weight percent or less of alkali ions such as K and Cs produces substantial amounts of higher alcohols (ref. 23, 24). For example, a Cu/ZnO catalyst with 0.4 mol% Cs when used at 310 °C and 7.6 MPa of H_2/CO (at a ratio of 0.45) has been found to produce a product mixture that contains about 40 wt% C_2^+ alcohols (ref. 25). However, the catalyst slowly deactivates. A waxy deposit of linear aliphatic hydrocarbon is found to coat a deactivated catalyst. The BET surface area of the catalyst also decreases but can be increased again by washing the catalyst with organic solvent. Thus, the high molecular weight deposits block the pores of the catalyst. It is conceivable that a small amount of alkali present unintentionally in the methanol synethesis catalyst could cause a similar production of high molecular weight deposits that eventually block the pores.

Deactivation by other causes

In the absence of poisons or other foreign substances, a Cu-Zn oxide catalyst still deactivates but very slowly, as a result of copper particle sintering. Reference 1 indicates that Polish workers have identified the main cause for deactivation of Cu-Zn-oxide catalyst being the decrease in the copper dispersion. The rate of sintering is temperature dependent. An extended x-ray fine structure (EXAFS) study shows that sintering of copper occurs readily at temperatures higher than 500 K (ref. 26). At temperatures above 573 K,

growth of ZnO crystallites also occurs and contributes to the sintering of Cu (ref. 25). Steam promotes sintering (ref. 16).

Removal of CO_2 from the feed stream is detrimental to the activity of the catalyst. In a laboratory test, the activity of the catalyst was reduced to 5% of the original value after 8 h of use without CO_2 (ref. 17). Surface analysis by Auger spectroscopy did not detect any carbon deposit. However, the color of the catalyst changed to pink, which is characteristic of large crystallites of copper.

Liquid Phase Process

A liquid phase synthesis process is under development in which the Cu-Zn oxide catalyst is suspended in an inert hydrocarbon liquid at about 523 K through which the feed gas is sparged. From the reports that describe the developmental effort, it is evident that the process suffers from deactivation of the catalyst (refs. 27, 28). The cause of deactivation has been identified (ref. 27). It was found that the catalyst in the pilot plant reactor deactivated at twice the rate as the one in the laboratory reactor. When the pilot plant catalyst was analyzed at different stages of deactivation, the residual activity was found to correlate linearly with the total amount of Fe and Ni deposited on the catalyst, and no correlation was found between the activity and the BET surface area, sulfur and chlorine concentration on the catalyst, Cu and ZnO crystallite size, the Cu/Zn or the Cu(I)/Cu(0) ratio. Analysis of the feed showed that it contained about 30 ppb(v) of $Fe(CO)_5$ and about 30 ppb(v) $Ni(CO)_4$. Thus these carbonyl compounds decomposed on the catalyst and blocked the active sites. That these carbonyl compounds were poisons was confirmed by the laboratory experiments in which the intentional addition of 1 ppm(v) of the compound was shown to cause distinctly faster deactivation.

The catalyst in this liquid phase process is also susceptible to poisoning by COS. COS reacts rapidly on the catalyst, and deposition of less than 0.6 wt% of S is sufficient to render the catalyst essentially inactive. This amount of sulfur corresponds to less than 3% monolayer coverage of the surface. Thus COS is a much more effective poison in the liquid phase than in the gas phase.

After discovering that the metal carbonyls were the primary cause for deactivation, these investigators proceeded to purify the feed stream carefully, and the lifetime of the catalyst was markedly improved. For example, after 1000 h of operation, the activity loss was only 20% compared with 60% before. However, deactivation was not eliminated. The residual activity now correlated with the surface area of the catalyst, and the rate of

deactivation was found to increase quite rapidly with increasing temperature. The data suggest that sintering is the cause of deactivation.

CATALYSTS DERIVED FROM Cu-RARE EARTH ALLOYS

It has been reported recently that active and selective methanol synthesis catalysts can be obtained by selective oxidation of Cu-rare earth alloys. These catalysts, such as those derived from $ThCu_6$, $CeCu_2$, $LaCu_2$ and $PrCu_2$, operate effectively with a CO/H_2 mixture (refs. 29-31).

In a typical experimental procedure, the catalysts are first activated in an atmosphere of CO and H_2. Pretreatment with hydrogen or N_2O has also been tried. In the used catalyst, the rare earth component is essentially all converted into the oxide, and the copper exists as very finely dispersed Cu crystallites. The extent of deactivation is quite substantial within hours of operation. It is believed that the rare earth metal is progressively oxidized in the synthesis mixture causing extrusion of submicroscopic particles of copper, which subsequently agglomerate resulting in loss of active area (ref. 30).

Exposure of the catalyst to O_2, H_2O, or CO_2 causes detrimental loss of catalytic activity. Exposure of the catalyst to CO_2 results in the conversion of the rare earth oxide to the stable carbonate. Although this is not accompanied by any apparent sintering of the detectable Cu crystallites, it probably causes the loss of very finely dispersed Cu particles by agglomeration that are too small to be detected. Oxygen exposure greatly suppresses the low-temperature methanol synthesis activity, but has much less effect on the high-temperature activity. It is probable that oxygen reacts with the surface carbonaceous residue to yield carbon dioxide, which then poisons the catalyst (ref. 31). Water lowers the activity of the catalysts, but the effect is less severe than that of O_2 or CO_2.

CONCLUSION

The low-temperature methanol synthesis catalyst of Cu-Zn oxide has a long lifetime under normal operating conditions, which is below 300 °C, and the feed contains less than 0.5 ppm of sulfur and chlorine and only a few parts per billion (ppb) of metal carbonyls. The catalyst is very sensitive to sulfur poisoning and is more sensitive to organic bound than inorganic bound sulfur. However, the ZnO component is a sulfur scavenger by forming Zn sulfide and sulfate. Deactivation by sintering of small copper crystallites, which is the active component, also occurs, but very slowly. The catalyst deactivates rapidly if CO_2 is removed

from the feed. Similar deactivation mechanisms apply to the catalysts for the gas phase and the liquid phase process. The laboratory catalysts derived from copper-rare earth alloys deactivate by exposure to O_2, CO_2, and, to a lesser extent, H_2O.

ACKNOWLEDGMENT

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