Catalyst Activity Maintenance Study for the Liquid Phase Dimethyl Ether Process

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OBJECTIVES

The co-production of dimethyl ether (DME) and methanol from syngas is a process of considerable commercial attractiveness. DME coproduction can double the productivity of a LPMEOH process when using coal-derived syngas [1]. This in itself may offer chemical producers and power companies increased flexibility and more profitable operation. DME is also known as a clean burning liquid fuel; Amoco and Haldor-Topsoe have recently announced the use of DME as alternative diesel fuel [2]. Moreover, DME can be a interesting intermediate in the production of chemicals such as olefins and vinyl acetate [3].

The current APCI liquid phase dimethyl ether (LPDME) process utilizes a physical mixture of a commercial methanol synthesis catalyst and a dehydration catalyst (e.g., γ-alumina). While this arrangement provides a synergy that results in much higher syngas conversion per pass compared to the methanol-only process, the stability of the catalyst system suffers. The present project is aimed at reducing catalyst deactivation both by understanding the cause(s) of catalyst deactivation and by developing modified catalyst systems. This paper describes our current understanding of the deactivation mechanism.

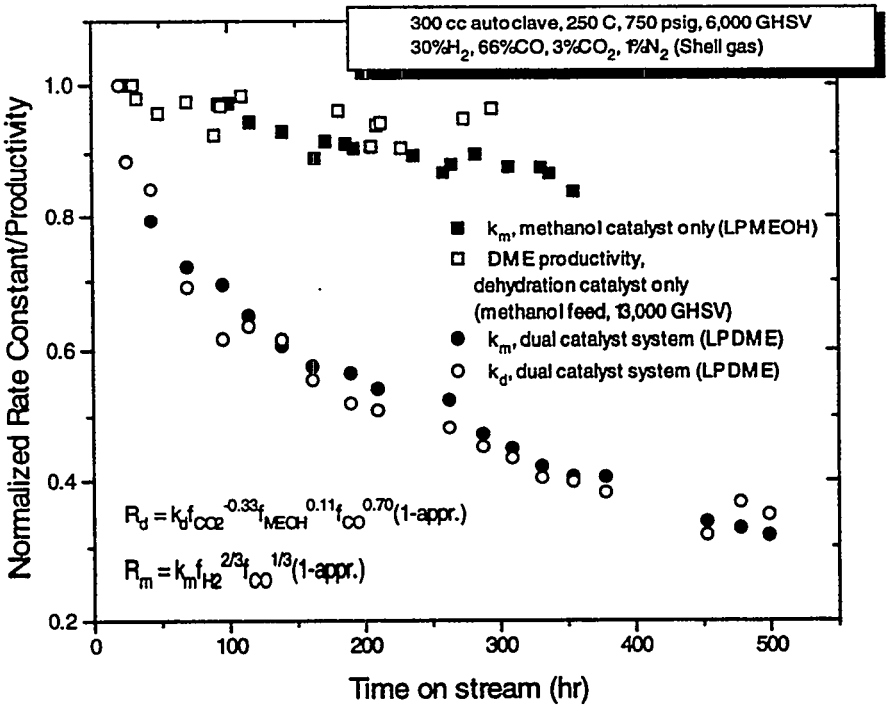
ACCOMPLISHMENTS

1. Introduction

Catalyst stability for LPMEOH, which uses only a methanol catalyst, is compared to that of a liquid phase dimethyl ether (LPDME) process, which uses a physical mixture of the same methanol catalyst and a γ-alumina (80:20 weight ratio) in Figure 1. Catalyst stability for a liquid phase dehydration experiment which uses γ-alumina only is also shown. All runs were carried out in a 300 cc slurry phase autoclave using powdered catalysts. The syngas used in both LPMEOH and LPDME run simulates that derived from a Shell-type gasifier. A 10% methanol in N_2 feed gas was used for the dehydration run.

For the LPMEOH and LPDME runs, the stability of the catalysts is expressed in terms of the apparent reaction rate constants (normalized to the initial values), calculated from the rate expressions shown in Figure 1. The subscript *m* refers to the methanol synthesis reaction, *d* to the methanol dehydration reaction, and *appr.* stands for the approach of the reaction to equilibrium, respectively. This methanol rate expression is the same as developed for the LPMEOH process while the dehydration rate expression was newly obtained by regression of the kinetic data of LPMEOH and LPDME experiments. They serve as a good semi-quantitative kinetic tool in the domain of the reaction conditions used in our experiments. For the dehydration run, the normalized DME productivity was used to describe the stability of the alumina.

Figure 1: Catalyst deactivation in different liquid phase processes



Both the methanol catalyst and the alumina are much less stable under the LPDME conditions than under LPMEOH conditions. Both catalysts undergo rapid deactivation for the first 80 hr or so, followed by a slow, continuous deactivation as long as the reaction proceeds. Although a stable productivity could be maintained in a commercial LPDME process by on-line catalyst withdrawal and addition, a stable catalyst system is still a preferred and ultimate solution to the problem. The work in the past year has gained a good understanding of the deactivation mechanism. Continuing work is focused on developing solutions to the rapid deactivation.

2. Investigation of the Possible Causes

Four major differences between the LPDME and the LPMEOH process have been identified. Each could be responsible for the catalyst deactivation under LPDME conditions.

First, the DME concentration is much higher in LPDME, e.g., typically 6% vs. <0.1% for LPMEOH. DME has been reported to disintegrate the texture of methanol catalyst [4]. It may also serve as a source of coke formation on the dehydration catalyst.

Secondly, the water concentration in LPDME is higher than that in LPMEOH due to the dehydration reaction. The water concentration depends upon syngas composition. It ranges from 0.15% to 1.3% in LPDME compared to LPMEOH (0.06%-0.2%). Hydrothermal sintering has long been known as a deactivation mechanism for methanol catalysts. The high water concentration may also deactivate the alumina by hydrating the alumina surface.

Thirdly, heavy oxygenates form under LPDME conditions. These heavy oxygenates can lead to coke formation which leads to the loss of the dehydration activity.

Finally, the physical/chemical interaction of alumina with the methanol catalyst could be a source of catalyst deactivation.

Based on these considerations, experiments were designed to investigate these possible causes individually. Each of these experiments is discussed below.

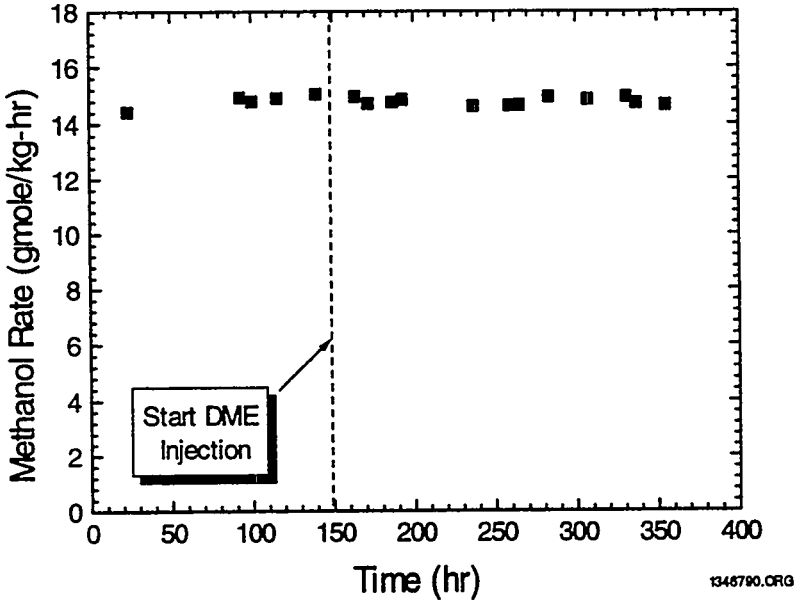
2.1. DME

DME was eliminated as the cause of methanol catalyst deactivation by cofeeding DME with syngas in an otherwise standard LPMEOH run. The experiment was conducted by first running methanol synthesis in a 300 cc autoclaves for 150 hr to establish a baseline. No alumina was present in the system. At 150 hr, the supplemental N_2 in the feed gas was replaced with DME at the same feed rate. The DME concentration in the reactor during this period, approximately 5 mol%, is typical of that observed during DME synthesis using the dual catalyst system.

The methanol production rate as a function of time is shown in Figure 2. Initial introduction of DME resulted in no change in the methanol production rate or the product distribution. This indicates that, at these conditions, the presence of DME has no influence on the kinetics of methanol synthesis. Most significant is the fact that the rate of decrease of the methanol activity during DME addition is comparable to that prior to the injection. This deactivation rate is much lower than rate of deactivation observed during LPDME synthesis using the dual

catalyst system. Thus, DME, per se, has no direct negative effect on the stability of the methanol catalyst.

Figure 2: Effect of DME addition on methanol catalyst stability
250 °C, 750 psig, GHSV=6,000 std.lit./kg-hr, Shell-type gas



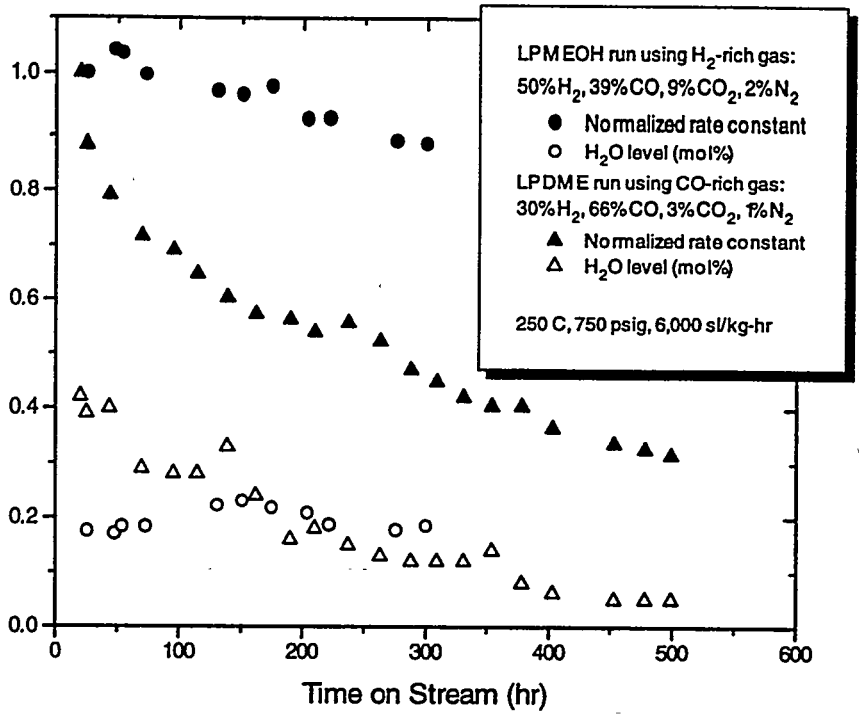
2.2. Water

The water level in both LPMEOH and LPDME reactions depends on the composition of the feed gas owing to the water gas shift reaction. This phenomenon prevents comparison at exactly the same conditions. However, one can run the two reactions at a similar water levels by using H_2-rich gas for LPMEOH and CO-rich gas for LPDME. The results of two experiments using this approach is shown in Fig. 3. It can be seen that, although the water levels in the two experiments are similar, the methanol catalyst is much less stable in the LPDME run. Thus, we infer that water, per se, is not the cause of the higher deactivation in the LPDME process. Although hydrothermal sintering is a known cause of methanol catalyst deactivation, it cannot be used as an explanation for the fast deactivation of the methanol catalyst under LPDME conditions.

2.3. Coking

Coke formation has been known to cause the deactivation of acidic catalysts such as alumina. Methanol and DME are unlikely the precursors of coke formation on the alumina surface under the temperature of LPDME reaction (250 °C), as the dehydration run using the alumina by itself and methanol as feed gas at 250 °C exhibited no sign of catalyst deactivation (Fig. 1). However, some heavier oxygenates, such as C2-C4 alcohols, methyl formate and acetate, and,

Figure 3: Stability of the methanol catalyst in LPMEOH and LPDME runs with a similar water concentration



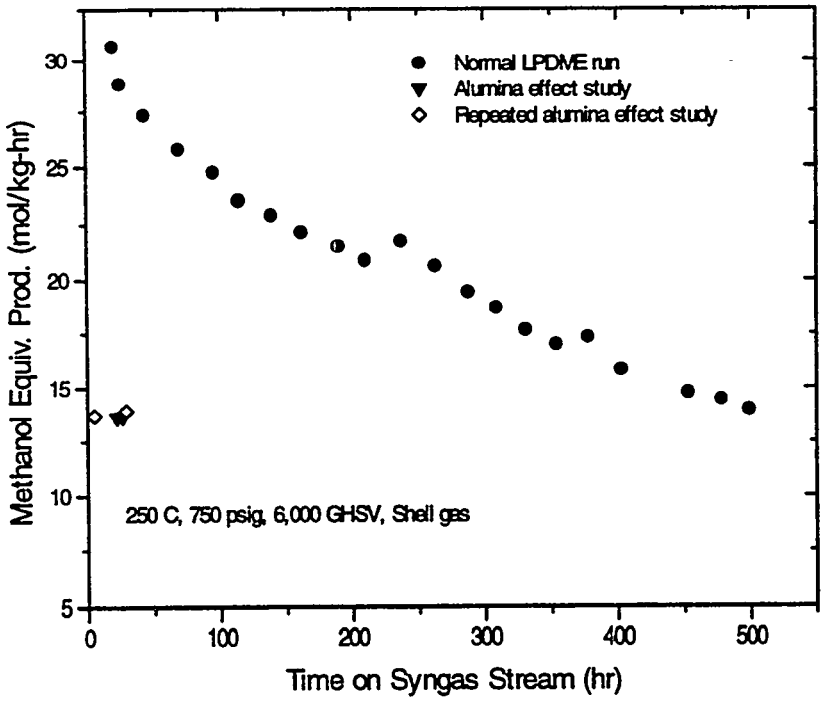
possibly, some nonvolatile species, are formed under LPDME conditions. These are possible coke precursors. Coke analysis of the alumina sample used in a LPDME run is difficult because the catalyst system contains well-mixed powders of the two catalysts of < 100 μm in size . A spent alumina pellet sample has been generated from a LPDME run using Robinson-Mahoney basket internals and pelletized methanol catalyst and alumina. At the present time, the coke analysis is obscured by the presence of residual slurry fluid (a hydrocarbon based mineral oil) in the sample. Therefore, the possibility of coking is as yet unresolved. Better extraction methods are being developed.

2.4. Alumina

The following experiment was designed to see if the presence of alumina per se results in the deactivation of the catalyst system. The standard catalyst mixture consisting of 80 wt.% of the methanol catalyst and 20 wt.% of the γ-alumina was loaded into a 300 cc autoclave. Following a normal catalyst reduction (using 2% H_2 in N_2), this catalyst system was left under flowing reduction gas (2% H_2 in N_2, 50 sccm/min.) at 250 °C for 117 hours with normal stirring. The activity of the catalyst system was then measured using the simulated Shell-type syngas to see if holding the two catalysts together at 250 °C had any effect on their activity. Since this scheme avoids exposure of the catalyst system to syngas and reaction products during the holding period, any effect can be attributed to the presence of alumina.

The activity of this catalyst mixture is compared in Figure 4 with that of a similar catalyst mixture from a normal LPDME life run. Merely holding the methanol catalyst together with the alumina at 250 °C for 117 hours resulted in a 55% drop in the methanol equivalent productivity. (The methanol equivalent productivity is defined as the methanol productivity plus 2 times of the DME productivity.) Judging by the rate constants calculated from the above mentioned methanol synthesis and methanol dehydration rate expressions, the methanol synthesis rate constant dropped by 68%, and the dehydration rate constant by 62%. This experiment was repeated. As shown in Fig. 4, the observation is reproducible. These results clearly indicate that there is a strong interaction between the methanol catalyst and the γ-alumina that deteriorates both catalysts. As will be discussed later, in a counter experiment deactivation of the methanol catalyst is low when the catalysts are not held in intimate contact.

Figure 4: The effect of the alumina on the stability of the catalyst system



Ideally, one would like to use a inert gas such as nitrogen or helium for the holding period. However, a previous experiment has shown that the methanol catalyst, when loaded by itself, deactivates irreversibly under flowing nitrogen (APCI zero grade) at 250 °C. In contrast, holding the methanol catalyst by itself at 250 °C under 2% H_2 in N_2 did not effect catalyst activity. Therefore, the reduction gas was used in the current alumina effect study. Since the normal LPDME run has a reducing atmosphere (high H_2 and CO concentration), it is plausible to say that the mechanism that is responsible for catalyst deactivation in the alumina effect study is also responsible for the catalyst deactivation under

the LPDME conditions. If there is any difference, it is the greater drop in the activity under the reduction gas (55% in methanol equivalent productivity) as compared to that under LPDME conditions (33%) for a similar length of time. This suggests that the interaction is more severe in the absence of the LPDME products.

3. Mechanistic Investigation

3.1. The nature of the interaction between the two catalysts

Figures 5 and 6 display the activity of methanol catalyst and dehydration catalyst, respectively, as a function of time on stream for two catalyst systems: the methanol catalyst plus γ-alumina and the methanol catalyst plus a ZnO-modified γ-alumina. The rate expressions described previously were used to calculate the rate constants. The methanol rate constant was adjusted to make the comparison between different catalyst systems on an equal basis. All the data were obtained under the standard conditions, i.e., 250 °C, 750 psig, 6000 GHSV, Shell-type gas, and a methanol-to-dehydration catalyst ratio of 80:20.

Figure 5: Methanol synthesis rate constant as a function of time on stream for different catalyst systems

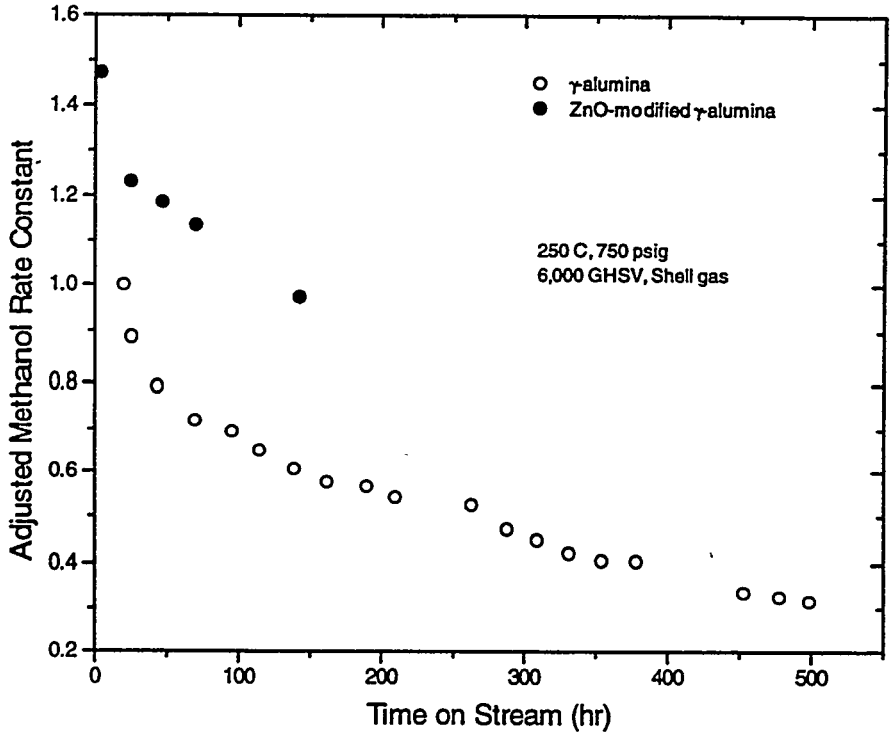
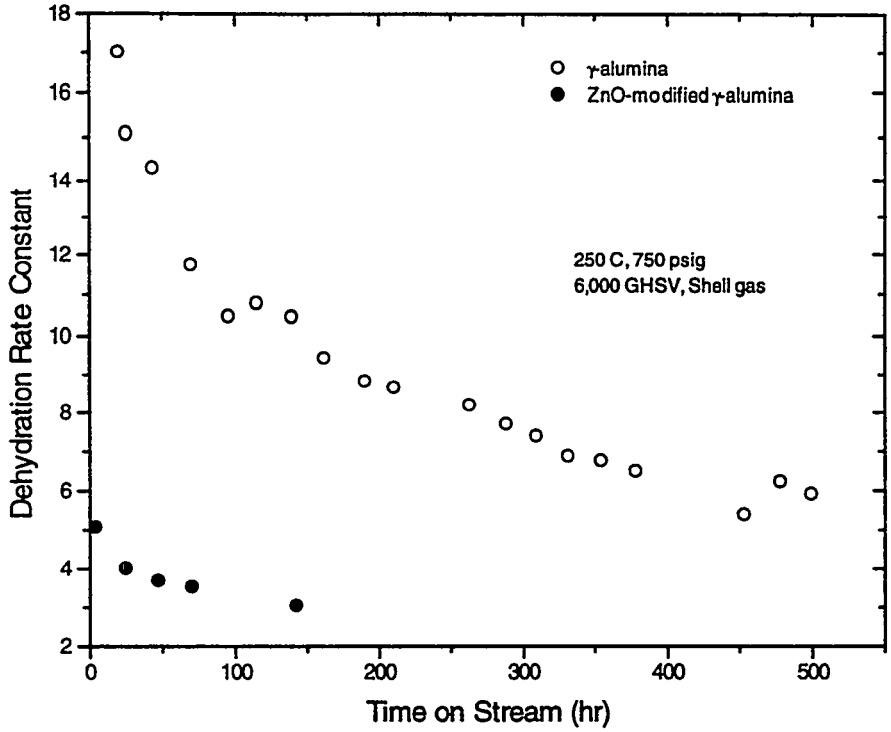


Figure 6: Dehydration rate constant as a function of time on stream for different catalyst systems

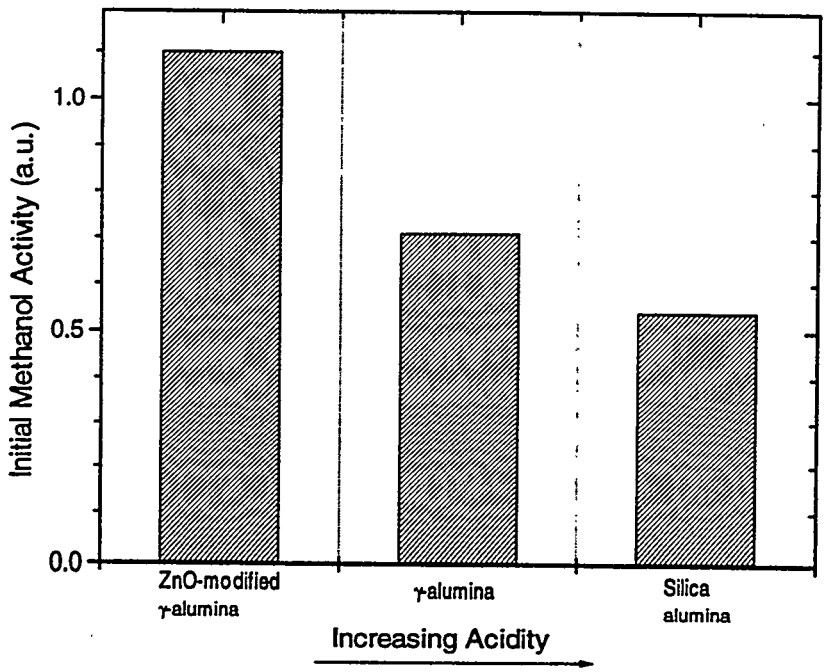


As shown in Figs. 5 and 6, the deactivation of both the methanol catalyst and the dehydration catalysts can be divided into two stages: a *initial*, fast deactivation followed by a stage of slower but continuous, *long term* deactivation. The division between the initial and long term deactivation is where the deactivation rate becomes almost constant. For the catalyst system containing virgin alumina, the initial deactivation period stops at ca. 80 hr on stream. For the system containing ZnO-modified alumina, it stops at ca. 40 hr. As discussed below, different mechanisms are operational behind these four different modes of catalyst deactivation.

A normal LPDME run in the lab starts with reduction of the methanol catalyst in the presence of a dehydration catalyst in the slurry. Apparently, the initial deactivation of the methanol catalyst occurred during the reduction, as suggested by the different initial activities of the same methanol catalysts in different catalyst systems (Fig. 5). Rapid deactivation continues into the early period when the system was on syngas stream. The magnitude of the initial deactivation and the length of this period appears to be a function of the acid strength of the dehydration catalyst. Figure 7 displays the initial deactivation of the methanol catalyst, measured by the methanol synthesis activity at 80 hours on syngas stream, as a function of different dehydration catalysts. Among them, the ZnO-modified γ-alumina possesses the weakest acidity since ZnO is a base. The silica alumina used in this study has the strongest acidity. It has exhibited higher activity toward isobutanol dehydration than γ-alumina in this lab. As

shown in Fig. 7, the initial deactivation of the methanol catalyst increases with increasing acid strength of the dehydration catalyst. This trend holds true for the other dehydration catalysts we have tested, including, other silica alumina, zeolitic materials, γ-alumina calcined and modified differently.

Figure 7: Correlation between the initial deactivation of the methanol catalyst and the acidity of dehydration catalysts



The long term deactivation of the methanol catalyst is not directly related to the acidity of dehydration catalysts. As shown in Figs. 5 and 6, although the two dehydration catalysts have different acidity, as indicated by the different dehydration activity, the deactivation rate of the methanol catalyst is similar for these two catalyst systems. A similar long term deactivation rate was also observed for the catalysts systems containing other dehydration catalysts mentioned above. This rate is ~ 0.082% hr^{-1}, a factor of 2 greater than that of the methanol-only system (0.045% hr^{-1}).

The pattern of the initial deactivation of dehydration catalysts varies from one system to another. In general, the deactivation occurs during the period of catalyst reduction and continues to the early hours on syngas stream. The strong acid sites appear to deactivate in this period. Moreover, the experiments using zeolitic materials demonstrate that the Brønsted acid sites deactivate very fast under LPDME conditions, dropping to a residual activity within 50 hours, regardless of the acid strength.

The long term deactivation of dehydration catalysts does not follow any clear pattern. The deactivation rate varies from one system to another. The higher dehydration activity, i.e., greater acidity, does not necessarily results in faster deactivation of the dehydration catalyst, or vice versa.

In summary, among the four different modes of catalyst deactivation, the initial deactivation of both methanol and dehydration catalysts is related to the acidity of the dehydration catalyst. The long term deactivation of both catalysts are not directly related to the acidity of dehydration catalysts. While the long term deactivation of the methanol catalyst exhibits a similar deactivation rate for different dehydration catalysts, the long term deactivation of dehydration catalysts does not follow a simple pattern.

The initial deactivation of the methanol catalyst is possibly *driven by the acid-base interaction* between the two catalysts, since it correlates with the dehydration activity (Fig. 7). Among the possible mechanisms are the inter-catalyst mass transfer and inter-catalyst solid state reaction. For instance, ion exchange could take place between Cu- and Zn-containing species from the methanol catalyst and the protons on the dehydration catalyst. Or the deactivation could be due to a reaction between ZnO (a base) in the methanol catalyst and the acid sites on a dehydration catalyst. The same acid-base interaction may also be responsible for the initial deactivation of dehydration catalysts. However, as discussed before, this deactivation could also be compounded by coke formation.

The mechanism for the long-term deactivation of both methanol and dehydration catalysts is not clear. For one thing, it is not directly related to the dehydration activity. The long term deactivation may still be due to inter-catalyst mass transfer or solid state reactions, but not likely acid-base in nature. For example, the migration of Zn- and Cu-containing species from the methanol catalyst to dehydration catalysts can be *driven by the concentration gradient* of these species between the methanol catalyst and dehydration catalysts. Note that most of the metal oxides tested as dehydration catalysts are also good catalyst supports with dispersing capability for metal, metal oxides, and salts, and the dispersing capability is not necessarily related to the acidity of the materials.

3.2. The role of the intimate contact between the two catalysts in the catalyst deactivation

The *driving force* discussed above alone may not be surficient to deactivate the catalysts. Unless the slurry fluid serves as mass transfer medium, the *intimate contact* between the two catalysts is necessary to provide the time and area for the mass transfer or/and reaction to take place. One can envision that the solid state reaction between the two catalysts can only occur when they touch each other and remain that way for a long enough time. The migration goes from the outer surface to the inner surface, requiring both contact time and area of the two catalysts. Under the slurry phase operation conditions, this intimate contact

can be provided by the collision between the catalyst particles, the attachment of small particles to the large ones, and the agglomeration of small particles. Collision and attrition continuously generate particles of smaller and smaller size, resulting in large and fresh (therefore active) contact area. This speculation is supported by the results from the following experiment.

This experiment was conducted using Robinson-Mahoney basket internals built to fit into a 300 cc autoclave. Methanol catalysts and alumina pellets were mixed together and loaded into the basket. The basket was submerged in a mineral oil in the autoclave and kept stationary during the run, while the oil was agitated to provide the mixing. The purpose of the R-M experiment is two fold. First, individual methanol catalyst and alumina samples can be obtained at the end of the run because it is easy to separate pellets. These samples were analyzed to elucidate the deactivation mechanism. Secondly, one would like to see if the change in the physical features of the reactor set-up would result in different deactivation behavior.

The reaction rate was mass transfer limited because of the use of pelletized catalysts. Therefore, the activity and stability of the catalyst system could only be checked in a subsequent run using the standard slurry phase operation conditions. For these runs, the spent pellets were ground into powders and re-loaded into the autoclave, now without the basket, to measure the activity. Two R-M runs were performed, one with a on-stream time of 500 hr, the other 120 hr. The activity of the spent catalysts from these two runs is listed in Table 1, along with that from a standard LPDME run (powdered catalysts). Again the rate expressions described above were used to calculate the rate constants.

Table 1: The activity of the spent catalysts from the LPDME runs using Robinson-Mahoney basket internals. Reaction conditions: 250 °C, 750 psig, Shell-type gas.

Run	MEOH Cat. :Al_2O_3	Time on Strm (hr)	MEOH Equiv. Prod. (mol/kg-hr)	Concentration (%) MEOH	DME	Rate Constant k_m	k_d
1st R-M run	82.2:17.8	508	28.1	1.59	6.13	2.7	10.7
2nd R-M run	80:20	127	27.1	2.74	4.87	3.1	7.0
Standard run	81.3:18.7	20	30.7	1.01	6.95	3.0	17.0
		115	23.6	0.83	4.89	1.9	10.8
		499	30.7	0.49	2.67	1.0	5.9

Some differences can be seen between the two R-M runs. Mainly, the sample from the second run exhibits higher methanol activity and lower dehydration activity. This difference is likely due to the experimental error in determining the actual ratio of the two catalysts in the ground samples. Given the experimental error, the same conclusion can be drawn from the two R-M runs. Judging by the rate constant, the spent methanol catalysts from the R-M runs have about the same activity as the fresh methanol catalyst in the standard run, and much higher activity than the methanol catalyst at a similar time on stream in the standard run. Therefore, both R-M runs indicate that the methanol catalyst is

stable under the R-M set-up. The dehydration catalyst deactivates in the R-M runs by 37-59%. Since the longer time on stream did not result in greater deactivation in the dehydration activity, it can be concluded that the deactivation of the dehydration catalyst occurred only in the earlier stage of the run (< 127 hr). That is, there is no long term deactivation of the dehydration catalyst under the R-M set-up.

Note that the Robinson-Mahoney reactor differs from a standard slurry phase reactor in that it does not have certain physical features of a slurry phase reactor such as mixing, powdered catalysts, and collision between catalyst particles. As described above, these features are likely to provide the intimate physical contact between the two catalysts, leading to catalyst deactivation by inter-catalyst mass transfer or/and inter-catalyst solid state reaction. In other words, without the intimate physical contact between the two catalysts, the methanol catalyst could be stable and the dehydration catalyst would not suffer long term deactivation.

The alumina suffered a initial deactivation even under the R-M set-up. This deactivation could be due to either inter-catalyst mass transfer or coking. If the inter-catalyst mass transfer is the reason, the slurry fluid must have served as the mass transfer medium. And apparently the methanol catalyst has some "free" Zn- and/or Cu-containing species to spare before its activity starts to suffer.

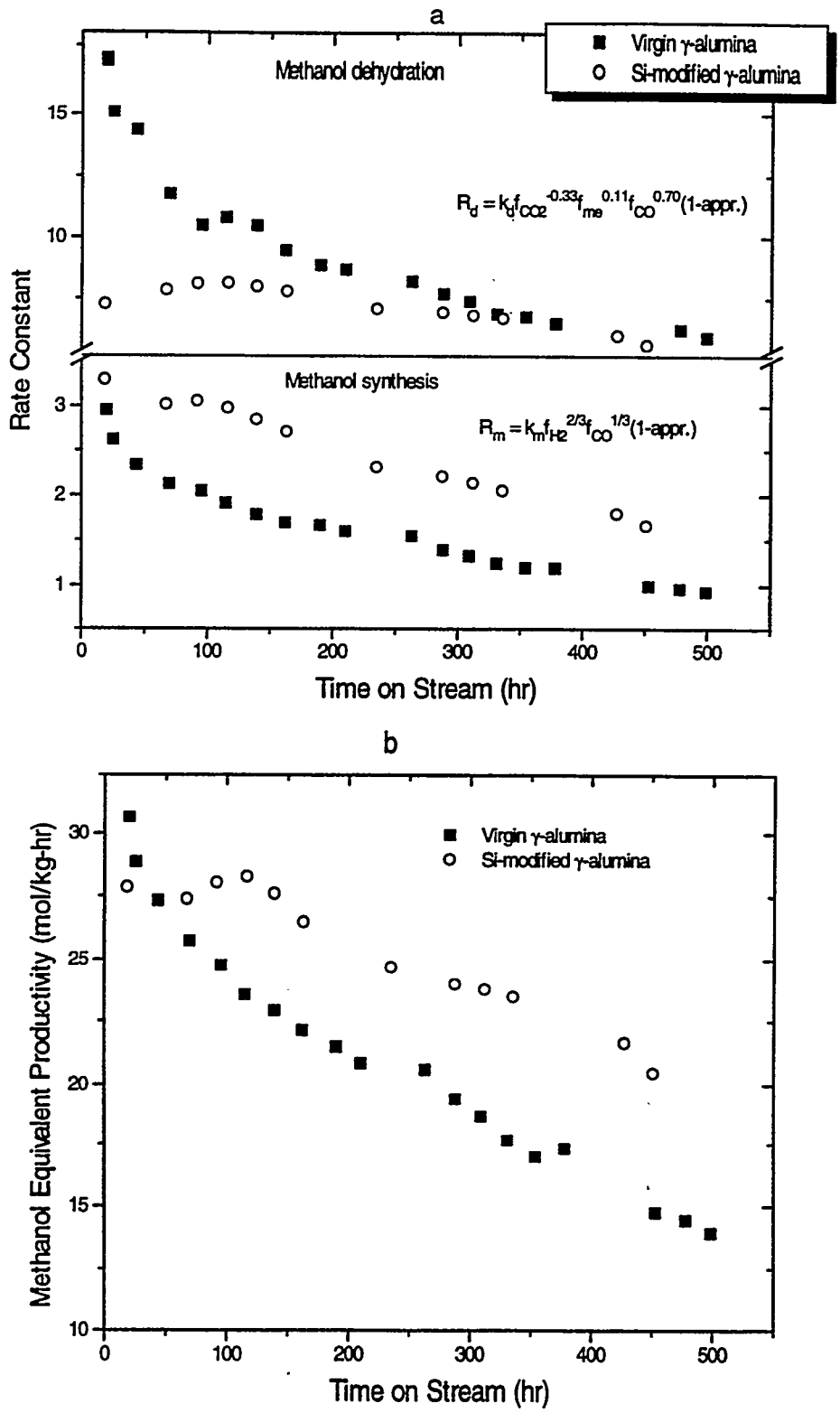
4. Progress in Solving the Problem

According to our current understanding of the deactivation mechanism, the problem can be solved by eliminating either the driving force for the inter-catalyst mass transfer/reaction or the intimate physical contact between the two catalysts. Efforts and progress are being made in both these directions.

Figures 8a and b provide an example how the stability of the catalyst system can be improved by reducing the driving force of the interaction between the two catalysts. In this example, the alumina was treated with a Si-containing compound to remove the strong acid sites. It can be seen from Fig. 8a that the modified alumina results in a much smaller initial deactivation of the methanol catalyst, or a 30% higher methanol synthesis activity. The long term stability of the methanol catalyst, however, is not improved by the modification.

The initial activity of the Si-modified alumina is lower than the virgin alumina due to the reduction in the number of acid sites by silica passivation. However, its long term deactivation rate is much lower than that of the virgin alumina. The combination of the high initial activity of the methanol catalyst with the slow long term deactivation of the dehydration catalyst results in a higher methanol equivalent productivity after the catalysts were on stream for 50 hr (Fig. 8b), as compared to the standard system (the methanol catalyst plus virgin γ-alumina).

Figure 8: The stability of the LPDME catalyst system: Si-modified γ-alumina vs. virgin γ-alumina



The rate of decrease in the productivity is also smaller, with a slope of 0.019 vs. 0.027 for the standard catalyst system, a 30% of improvement. The stability of this catalyst system is not all that could be desired because of the poor long term stability of the methanol catalyst.

CONCLUSIONS

This investigation shows that high level of water and DME under the LPDME conditions has no direct effect on the deactivation of the catalysts. An interaction between methanol and dehydration catalysts has been identified as the cause of the deactivation of both catalysts. In the initial stage, this interaction is predominantly associated with the strong acid sites on the dehydration catalyst, resulting in a fast, initial deactivation of the methanol catalyst and the elimination of the strong acid sites on the dehydration catalyst. The slower, long term deactivation of both catalysts are not directly related to the acid-base properties of the catalyst system, but to an interaction of yet uncertain nature. The initial deactivation of the methanol catalyst can be avoided by passivating the strong acid sites on a dehydration catalyst. Furthermore, except for the initial deactivation of the dehydration catalyst, both catalysts can be stable if the intimate contact between them can be avoided. Efforts and progress are being made to improve the stability of the catalyst system based on this understanding.

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