NOVEL DEVELOPMENTS AND ENHANCEMENTS IN METHANOL SYNTHESIS

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ABSTRACT

Extensive experimental work was done to clarify the various fundamental aspects of methanol synthesis technology. The methanol synthesis chemistry has been firmly established and experimental data to support the reaction scheme has been obtained. Novel processes have been developed and tested for the regeneration and post-treatment of copper based catalysts for methanol synthesis. An effective method for the co-production of dimethyl ether and methanol using a new dual catalysis approach has been established. This approach enabled outstanding hydrogenation rates to be obtained while at the same time maintaining good selectivity and catalytic activity. Even though all the investigations have been made on the liquid-phase methanol synthesis process, the results with regard to catalyst regeneration and post-treatment will also be valid for the vapor-phase synthesis process.

INTRODUCTION

Enhanced research efforts in recent years have enabled significant progress to be made in our understanding of the science and technology of the catalytic synthesis of methanol from syngas. In particular, research focused on the liquid phase methanol synthesis process has led to breakthroughs, not only in new process development and in the enhancement of existing processes, but also in improving our understanding of the fundamentals of methanol synthesis.

The LPMEOH™ process was originally developed by Chem Systems, Inc. in 1975 [1]. This process was especially attractive because it offered better heat transfer and reactor thermal stability characteristics as compared to earlier processes. Various aspects of this new process, including thermodynamics and phase equilibria [2,3], global reaction kinetics and pore diffusional limitations [4,5,6], and external mass transfer limitations in a mechanically agitated slurry reactor [7,8], have been investigated to date.

The LPMEOH™ process offers distinct advantages in (a) achieving very high selectivity for methanol, (b) enhancing the heat transfer characteristics, and (c) enabling the use of CO-rich syngas feed.

There are, however, a few areas of concern with the liquid phase methanol process, such as, poor mass transfer, especially gas-to-liquid mass transfer, poor methanol productivity per unit volume of reactor, and reduced catalyst life.

This paper focuses on the following factors that have a direct bearing on the economics of the overall process:

(a) enhancement of methanol production rate by reducing the combined mass transfer and thermodynamic equilibrium limitations,

(b) in-situ regeneration of deactivated catalyst, and

(c) improvement of catalyst life by post-treatment of reduced catalyst.

Even though all the experimental investigations were made on the liquid-phase methanol synthesis process, the results with regard to catalyst regeneration and post-treatment will also be valid for the vapor-phase synthesis process.

SYNTHESIS CHEMISTRY

In our earlier work [9,10], the chemistry of syngas conversion to methanol has been discussed and firmly established. The conclusions were based on both material balances and thermodynamic equilibrium calculations. The philosophy was that the chemistry must be consistent with the direction of the reversible reactions as determined by calculations of changes in Gibbs free energy and with the experimentally obtained material balances. A brief discussion of the methanol synthesis chemistry has been summarized below.

For convenience, three different cases may be considered.

Case 1. CO-rich or Hydrogen-rich Syngas

This case covers a range of feed gas compositions typical of products from Lurgi and Koppers-Totzek type gasifiers (i.e., both hydrogen rich and CO-rich syngas). The gas normally contains 2 to 12 mole percent Carbon dioxide. Then, the chemistry for the synthesis of methanol can be written as:

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

The synthesis is therefore based on the hydrogenation of carbon dioxide and the forward water gas shift reaction. The direction of the water gas shift reaction was determined by comparing the calculated Gibbs free energy change with experimental measurements of fugacities in the liquid phase. The water that is produced is not detrimental to the overall process at least from the kinetic standpoint, since the fast forward water gas shift reaction consumes water to produce more reactants for the main synthesis reaction.

Case 2. CO-free Syngas

It has been reported that the methanol formation rate is quite low when there is absolutely no carbon monoxide in the syngas feed. This experimental observation led some investigators to suspect that methanol synthesis proceeds by the hydrogenation of carbon monoxide rather than by the hydrogenation of carbon dioxide. However, experimentally obtained material balances as well as thermodynamic equilibrium studies indicated that the carbon dioxide hydrogenation route is still consistent. The only difference from the previous case was in the direction of the water gas shift reaction.

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (3)$$

$$CO_2 + H_2 = CO + H_2O \qquad (4)$$

The low rate of methanol formation may be attributed to the following two factors: (1) the two reactions are competing for the common reactants, and (2) the selectivity for methanol is very low and water accumulates sufficiently to cause thermodynamic equilibrium limitations to the methanol synthesis reaction. Even with the CO-free syngas feed like the current case, CO is still produced in the reactor and is easily detected in the exit gas stream.

Case 3. Carbon dioxide-free Syngas

The rates of methanol formation have also been reported to be quite low without carbon dioxide in the syngas feed. Based on chemical equilibrium calculations as well as material balances and other experimental observations, the following synthesis route was found to be consistent:

$$2CO = CO_2 + C \qquad (5)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (6)$$

$$CO + H_2O = CO_2 + H_2 \qquad (7)$$

The key point to be noted is that carbon dioxide is still formed (detectable in the exit gas stream) by a precursor or pilot reaction, such as reaction (5). Since there is no other source for carbon atoms than CO in the feed, it is very safe to assume that the carbon atoms in the carbon dioxide must have come from the carbon monoxide. However, there are two sources of oxygen atoms, viz, ZnO and CO. If zinc oxide is indeed the source of oxygen atoms, then reaction (5) would be replaced by

$$ZnO + CO = CO_2 + Zn \qquad (8)$$

Regardless of whether reaction (5) or reaction (8) takes place as the precursor reaction, damage to catalytic activity would result. Declining catalytic activity was indeed experimentally observed [10].

It is obvious that reactions (6) and (7) are self-sustaining as long as the precursor reaction produces small amounts of carbon dioxide during the initial stages. It is evident that the methanol formation rate would be low under these conditions.

Summary

In order to ensure and maintain a high methanol productivity over $Cu/ZnO/Al_2O_3$ catalysts it would be necessary to have hydrogen, carbon monoxide and carbon dioxide in the feed stream. Hydrogen must be present in the feed for the hydrogenation reaction to proceed. Carbon monoxide must be present in the feed to enable the forward water gas shift reaction to take place. Carbon dioxide is necessary in order not to damage the catalyst and to provide sufficient reactants.

CATALYST REGENERATION

It was observed that the catalyst crystallites (to be specific, the copper crystallites) tend to grow in size with use under reactive conditions. A simultaneous decline in catalytic activity was also noticed. If there is indeed a cause-effect relationship between the two, any catalyst regeneration process must have the reduction of the crystallite sizes as a goal. A novel process has been developed [11] to effect such a reduction by cyclic treatment to induce phase changes.

The size distribution of copper crystallites was obtained by X-ray diffraction crystallography [12] coupled with line profile analysis. It was noticed [14] that for the freshly reduced EPJ-19 ($Cu/ZnO/Al_2O_3$) catalyst, the distribution is nearly uni-modal and skewed to the left. After 200 hours of use, in a CO-free syngas environment, the distribution was tri-modal, and the average size had increased significantly over that observed for the freshly reduced catalyst. The same catalyst batch was subjected to the newly developed process and the size distribution was once again determined [14]. A comparison of the size distributions for the deactivated and regenerated catalysts as well as the original catalyst seems to qualitatively support Ostwald's theory of crystal size growth.

The in-situ regeneration process was successful in reducing the average copper crystallite sizes. This led to the next question: does this reduction in crystallite size go hand-in-hand with a recovery in lost catalytic activity? Comparative activity data have been reported [14] for mildly deactivated catalyst, regenerated catalyst after one cycle of treatment, and regenerated catalyst after two consecutive cycles of treatment. Experiments were carried out under nominally similar conditions using a CO-rich syngas mixture as feed gas. The reactivity increased from 16.081 mol/kg cat-h, to 17.323 after one cycle, and then to 18.495 after two cycles (amounting to 98% of the activity of the freshly reduced catalyst (18.798 mol/kg cat-h)).

The new regeneration process is especially significant because:

(a) it can be very effectively implemented without making design changes in the reactor system and without opening the reactor proper.

(b) the experiments prove that the loss in catalytic activity is largely due to the increased crystallite sizes and, if the average crystallite size is properly reduced, then the lost activity can be restored.

It should be noted that this newly developed process would be applicable to vapor-phase synthesis catalysts as well because the catalyst itself and the chemistry are essentially the same.

POST-TREATMENT OF CATALYST

The development of a post-treatment step for the methanol synthesis catalyst was essentially guided by the need for (a) improving the mechanical strength of the catalyst, (b) protecting the mineral matter of the catalyst from being leached out when used in the liquid phase process, and (c) slowing down the catalyst crystallite size growth.

Catalyst post-treatment is based on the formation of $ZnCO_3$ by:

$$ZnO + CO_2 = ZnCO_3 \tag{9}$$

Zinc oxide is a major component of $Cu/ZnO/Al_2O_3$ catalysts. Our earlier studies [12] indicated that ZnO is vulnerable to attack by water present in the bulk phase. On the other hand alumina is vulnerable to attack by microscopic contact with water. The equilibrium constant for reaction (9) is:

$$\begin{aligned} K_a &= 2015.251 \text{ at } 25\text{ C and } 1 \text{ bar} \\ &= 0.01367 \text{ at } 237 \text{ C and } 1 \text{ bar} \end{aligned} \tag{10}$$

This means that the formation of zinc carbonate is thermodynamically favored at normal conditions, and at process temperature, it will be favored when the partial pressure of carbon dioxide is higher than 1/0.01367 atm.

Extensive studies have been made to develop a process [13] that can be used to effectively post-treat the reduced catalyst. It was found that the post-treated catalyst is better able to retain its activity under nominally identical reactive conditions.

CO-PRODUCTION OF DIMETHYL ETHER AND METHANOL

It was found in our earlier work [13], that thermodynamic equilibrium limitations on the overall reaction rate become quite serious when the reaction is influenced by mass transfer resistances. This situation is caused by the accumulation of methanol in the reactor which drives the system closer to the chemical equilibrium composition. This reduces the kinetic driving forces. Therefore, it was suggested that the methanol that is produced be removed or be converted into some other chemical species, in order to reduce the methanol concentrations in the reactor.

One method would be to promote the co-production of dimethyl ether (DME). This would consume some of the methanol that is produced in the reactor thereby reducing the burden of reaction equilibrium. The chances of success are very good as long as one can achieve DME co-production with the synthesis of methanol using a suitable second catalyst of high activity. A novel process has been developed based on this philosophy, in which both methanol and dimethyl ether are co-produced in the liquid phase in a single stage reactor through dual catalysis. Dual catalysis has seldom been used before, usually because of incompatibility of the two catalysts and/or products. Therefore, the significance of the new process may be substantial not only from the commercial standpoint, but also from the scientific standpoint.

Activity data for the co-production of dimethyl ether and methanol were experimentally obtained [14] from a single-stage, mechanically stirred slurry reactor. It was evident from the results that the overall reaction rates were strongly limited by thermodynamic equilibria. The rates of DME production were very promising. Under the same experimental conditions, it was found that the hydrogenation rates were 57% higher with the co-production approach than when the single methanol synthesis catalyst was used alone. This comparison is based on a mole balance for CH_3- production.

The co-production of dimethyl ether and methanol may be represented as follows:

$$CO_2 + 3H_2 = CH_3OH + H_2O \tag{11}$$

$$CO + H_2O = CO_2 + H_2 \tag{12}$$

$$2CH_3OH = CH_3OCH_3 + H_2O \tag{13}$$

It would appear that water, which is a byproduct of both reactions (11) and (13), would accumulate in the reactor and have a detrimental effect on the overall process. However, this is not the case, as long as a normal syngas feed (containing hydrogen, carbon monoxide, and carbon dioxide) is used. This is because reaction (12) proceeds faster than the other two and awaits the supply of in-situ produced H_2O. This is one of the strongest advantages of the liquid-phase methanol synthesis process and is the reason for high selectivity for methanol. The co-production process is also very selective with respect to the hydrogenation and very little water is produced in net amount.

CONCLUSIONS

The results of our work may be summarized as follows.

(1) The global chemistry by which methanol is synthesized from syngas on $Cu/ZnO/Al_2O_3$ catalysts has been firmly established. Experimental data under various conditions have been found to be consistent with the proposed scheme.

(2) A novel process for the regeneration of catalysts has been developed and found to be effective in reducing the crystallite sizes almost back to normal. It was also found that a strong correlation exists between increase in crystallite sizes and drop in catalytic activity under normal operating conditions.

(3) A new process for the post-treatment of methanol synthesis catalysts has been developed. The process was effective in maintaining not only the catalytic activity but also the mechanical and chemical strength of the catalyst.

(4) A novel process has also been developed for the co-production of dimethyl ether and methanol. This process was found to be very efficient for the hydrogenation of syngas. The reactivity was outstanding and good selectivity was obtained using only a single stage reactor. It was also a scientifically successful use of dual catalysis.

ACKNOWLEDGMENTS

This work was fully supported by the Electric Power Research Institute, under Research Contracts, RP-2146-02/8003-11/317-6. The authors wish to thank Conrad J. Kulik, EPRI Project manager, for his advice and for sharing his thoughts with us. Thanks are also due to United Catalysts, Inc., for providing us with a supply of EPJ catalysts, and to BASF, for their BASF S-3.85 catalyst.

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