CATALYST ACTIVITY MAINTENANCE FOR THE LIQUID PHASE SYNTHESIS GAS-TO-DIMETHYL ETHER PROCESS

PART II: DEVELOPMENT OF ALUMINUM PHOSPHATE AS THE DEHYDRATION CATALYST FOR THE SINGLE-STEP LIQUID PHASE SYNGAS-TO-DME PROCESS

FINAL

Topical Report

Prepared by Xiang-Dong Peng

Contractor:

AIR PRODUCTS AND CHEMICALS, INC. Allentown, PA 18195

May 2002

Prepared for the United States Department of Energy Under Contract No. DE-FC22-94 PC93052

NOTE: AIR PRODUCTS DOES NOT CONSIDER ANYTHING IN THIS REPORT TO BE CONFIDENTIAL OR PATENTABLE.

TABLE OF CONTENTS

AE	BSTRACT	1
1.	INTRODUCTION	2
	1.1. Catalyst Activity Maintenance in Single-Step Syngas-to-DME Processes	2
	1.2. Preparation of Aluminum Phosphate as Catalysts – Literature Review	4
2.	EXPERIMENTAL	7
	2.1. Life Test Experiments	7
	2.2. Catalyst Preparation	8
3.	STABLE AIPO4-CONTAINING DUAL CATALYST SYSTEMS	9
	3.1. Stable Results	9
	3.2. Preparation of Aluminum Phosphate Samples with Good Activity and Stability	16
	3.2. Rate of Catalyst Deactivation as a Function of Reaction Temperature	18
4.	INVESTIGATION OF PREPARATION PARAMETERS	20
	4.1. Starting Aluminum Salts	20
	4.2. Precipitation Conditions	21
	4.3. Al:P Ratio	21
	4.4. Maturing Time of the Precipitate	22
	4.5. Washing Procedures	23
	4.6. Calcination Temperature and Ramp Rate	26
	4.7. Post Treatment: Nitridation	28
	4.8. Aluminum Phosphate in Supported Form	29
5.	MECHANISTIC DISCUSSION	31
	5.1 Hypothesis 1: Uniformity	31
	5.2 Hypothesis 2: Contamination	32
6.	SUMMARY AND RETROSPECT	33
RF	EFERENCES	34

34

ABSTRACT

At the heart of the single-step liquid phase syngas-to-DME process (LPDMETM) is a catalyst system that can be active as well as stable. In the Alternative Fuels I program, a dual-catalyst system containing a Cu-based commercial methanol synthesis catalyst (BASF S3-86) and a commercial dehydration material (γ-alumina) was demonstrated. It provided the productivity and selectivity expected from the LPDME process. However, the catalyst system deactivated too rapidly to warrant a viable commercial process [1]. The mechanistic investigation in the early part of the DOE's Alternative Fuels II program revealed that the accelerated catalyst deactivation under LPDME conditions is due to detrimental interaction between the methanol synthesis catalyst and methanol dehydration catalyst [2,3]. The interaction was attributed to migration of Cu- and/or Zn-containing species from the synthesis catalyst to the dehydration catalyst. Identification of a dehydration activity was elusive. Twenty-nine different dehydration materials were tested, but none showed the desired performance [2].

The search came to a turning point when aluminum phosphate was tested. This amorphous material is prepared by precipitating a solution containing $Al(NO_3)_3$ and H_3PO_4 with NH_4OH , followed by washing, drying and calcination. The aluminum phosphate catalyst has adequate dehydration activity and good stability. It can co-exist with the Cu-based methanol synthesis catalyst without negatively affecting the latter catalyst's stability.

This report documents the details of the development of this catalyst. These include initial leads, efforts in improving activity and stability, investigation and development of the best preparation parameters and procedures, mechanistic understanding and resulting preparation guidelines, and the accomplishments of this work.

1. INTRODUCTION

1.1. Catalyst Activity Maintenance in Single-Step Syngas-to-DME Processes

Driven by energy and environmental needs, single-step production of DME from synthesis gas (or syngas, a mixture of H_2 and CO) has received considerable attention in recent years. The advantage of the single-step process is the high syngas conversion per pass compared to, for example, the traditional two-step process in which methanol is produced from syngas in a reactor over a methanol synthesis catalyst, then converted into DME in a subsequent reactor over a dehydration catalyst. At the heart of the single-step DME process is a catalyst system that possesses both methanol synthesis and methanol dehydration activity. The success of the development of this process depends on an active as well as stable catalyst system.

There are two types of single-step syngas-to-DME catalysts:

- 1. The first type, the so-called dual catalyst system, consists of a physical mixture of a methanol synthesis catalyst and a dehydration catalyst. The methanol catalyst is normally a Cu-based commercial catalyst, and the dehydration catalyst is selected from solid acid materials such as γ -alumina and zeolites. In fixed- or fluidized-bed applications, the powders of the two catalysts can be mixed and then formed into pellets or beads, or separate pellets or beads of the two catalysts can be prepared. The pellets can be placed in a fixed-bed reactor either in a well-mixed form or in a layer-by-layer arrangement. In the slurry phase application, a powder mixture of the two catalysts can be directly used.
- 2. In the second type of syngas-to-DME catalyst, the two functionalities are built into a single catalyst. This has been achieved either by co-precipitating methanol synthesis and dehydration components together to form one catalyst, or by precipitating methanol synthesis components onto an existing, high-surface-area solid acid material.

The single-step syngas-to-DME process can be conducted either in the gas phase using a fixedor fluidized-bed reactor, or in the liquid phase using a slurry reactor with an inert liquid medium. However, catalyst activity maintenance remains a major challenge to both operations, especially when a dual catalyst system is used.

A 1982 Mobil patent [4] discloses a gas phase process for DME production to be used in conjunction with an integrated gasification combined cycle power plant. Examples in the patent show that the catalyst, consisting of a Cu-, Zn-, Cr- or Al-based methanol catalyst and γ -alumina as the dehydration component, requires frequent regeneration, in some cases on a daily basis.

A 1983 Mobile patent [5] discloses a two-component catalyst for direct conversion of syngas into DME in a single gas phase reactor. The catalyst pellets were made from a powder mixture containing a Cu, Zn and Al coprecipitated methanol synthesis catalyst and an acidic dehydration component selected from γ -alumina, zeolites, phosphates and other solid acid materials. The γ alumina-containing catalyst system was shown in the examples. The catalyst deactivated rapidly under the reaction conditions (315°C, 100 atm). Regeneration using oxygen was demonstrated to some extent for several cycles, but eventually the catalyst died after 50 days on stream.

Similar deactivation was also observed by other researchers [6]. A bifunctional catalyst system, prepared by pressing a powder mixture of a Cu-Zn-Al methanol synthesis catalyst and γ -alumina into pellets, underwent rapid deactivation at 275°C under the single-step syngas-to-DME conditions. Oxidative regeneration results in partial recovery of the catalyst activity, followed by more rapid deactivation.

Constant DME productivity was reported in an article by G. Cai et al. [7]. The reaction was conducted in a fixed-bed reactor using a catalyst made of a powder mixture of a methanol synthesis catalyst and modified H-mordenite. However, this apparent constant productivity was maintained by increasing the reactor temperature from 240 to 320°C over a period of 2100 hours. Thus, while constant activity was maintained, catalyst deactivation occurred.

Our catalyst stability study under the DOE Alternative Fuels Program [2,3] showed that, when a powdered physical mixture of a commercial methanol synthesis catalyst and γ -alumina were used in the liquid phase DME process (LPDMETM), rapid deactivation of both catalysts occurred.

The catalyst stability problems described above relate to the very concept of single-step syngasto-DME itself. First, it can be due to the great amount of heat released from high syngas conversion, especially in the case of fixed-bed operations, because the methanol synthesis reaction is highly exothermic. When a methanol synthesis catalyst is used by itself in a oncethrough operation in a fixed bed, its activity normally cannot be fully utilized, because the heat released from higher syngas conversion cannot be adequately dissipated. Since the single step syngas-to-DME process provides much higher syngas conversion per pass, one would expect more severe methanol catalyst deactivation in a fixed-bed operation if the potential conversion of the process is to be completely utilized.

Second, introduction of the acid functionality into the catalyst system introduces additional problems. Strong acid sites will cause coke formation, leading to deactivation of the dehydration catalyst. High temperature in a fixed-bed reactor caused by high syngas conversion, hot spots, and temperature over-shooting will increase the severity of this problem.

The third problem is the compatibility between the methanol synthesis catalyst and the dehydration catalyst when a dual catalyst system is used. Our previous work [2,3] demonstrated that the rapid and simultaneous deactivation of methanol synthesis and dehydration catalysts is caused by a novel mechanism, namely, an interaction between the two catalysts. The problem is again related to the acidity of the dehydration catalyst — more rapid deactivation is observed when the dehydration catalyst contains acid sites of greater strength. This detrimental interaction may also occur in the gas phase operation when intimate contact between the two catalysts is provided [8].

In summary, three catalyst stability problems are associated with dual-catalyst systems used in single-step syngas-to-DME processes:

- 1) Sintering of the methanol catalyst in fixed-bed operation,
- 2) Coke formation on dehydration catalysts, and
- 3) Detrimental interaction between the methanol synthesis and methanol dehydration catalysts.

The first problem is related to heat management and can be circumvented by employing liquid phase reaction technologies. Better heat management can be attained in a slurry phase reaction because of the presence of an inert liquid medium and better mixing. The second and the third problems are related to the acidity of the dehydration catalyst in a dual-catalyst system. Therefore, a dehydration catalyst with the right acidity is crucial to the stability of a dual-catalyst system. This understanding led us to screen different solid acid materials [2]. Aluminum phosphate was the one that gave us stable catalyst performance. This report covers our work on developing aluminum phosphate as the dehydration catalyst for our LPDME application.

1.2. Preparation of Aluminum Phosphate as Catalysts – Literature Review

Amorphous aluminum phosphate, either in bulk or supported form, has long been used as catalyst supports or catalysts for a variety of reactions such as dehydration, isomerization, alkylation, hydrotreating and cracking reactions [9,10]. Aluminum phosphate contains two types of acid sites. As shown in Figure 1, the proton in the OH groups attached to phosphorus serves as a Bronsted acid, while the unsaturatedly coordinated aluminum ions serve as a Lewis acid.



Bronsted acid Lewis acid Figure 1: Acid Sites in Aluminum Phosphate

The performance of an aluminum phosphate catalyst is sensitive to its preparation. A review of this subject can be found in Reference 11. The following is a brief review of the patent literature on some unique preparation procedures and the applications of the materials.

High-surface-area aluminum phosphate can be prepared by forming high-surface-area-aluminum phosphate gels as the intermediate [12]. The gel is made from an aqueous solution of aluminum chloride and phosphoric acid with ethylene or ammonium hydroxide as the gelling reagent. The preparation requires careful control over pH, temperature and other conditions so that a hydrogel can be formed during precipitation. The washing procedure and the medium also play important roles in amount of surface area of final materials. The gel loses its surface area readily on contact with water. The catalyst is claimed to be good for dehydration of alcohols to olefins or ethers and oil cracking.

The ratio of aluminum to phosphorus is another important factor in determining the performance of aluminum phosphate catalysts. Stoichiometric aluminum phosphate contains one aluminum atom for each phosphorus atom (AlPO₄). If the ratio is less than one, phosphoric oxide phases (e.g., P_2O_5) will appear, and the catalyst will contain a high population of Bronsted acid sites. If the ratio is greater than one, a mixture of alumina-aluminum phosphate will be formed, meaning more Lewis acid sites with greater strength (those from the alumina phase). Therefore, the Al:P ratio is an effective way to tune the acid property of an aluminum phosphate catalyst. For example, alumina-aluminum phosphate mixtures with aluminum phosphate ranging from 35 to 85 wt % have been prepared [13] by reaction in an aqueous medium of aluminum alkoxide with an inorganic or organic phosphorous-containing acid or soluble salt. The material was demonstrated as a catalyst support for the preparation of a platinum reforming catalyst.

An alternative and more economic way to prepare alumina-aluminum phosphate is described in a 1978 patent [14]. It produces thermally stable composite precipitates containing aluminum phosphate (40 to 90 mol %) and alumina (10 to 60 mol %). These materials are prepared by co-feeding an aqueous solution of Al cations (from aluminum nitrate, chloride, or sulfate) and PO₄ anions (from phosphoric acid) and a neutralizing medium, either ammonia gas or ammoniabased materials such as ammonium hydroxide, ammonium carbonate, ammonium bicarbonate, and urea to a common vessel, followed by filtration, washing, drying, and calcination. The scheme of neutralization is designed to provide a constant pH environment (7 to 10) for precipitation, which is claimed to be necessary for good thermal stability of the final products. The final materials have surface areas ranging from 100 to 200 m²/g and pore radii from 75 to 150 Angstroms.

Another preparation for alumina-aluminum phosphate is described in a 1980 Exxon patent [15]. The precipitates are formed by reaction of a mixture of aluminum alkoxide and an organic phosphate (e.g., trialkyl or triaryl phosphate) in the presence of moist air, followed by drying and calcination. The aluminum phosphate in the final product may range from about 10 to about 90% by weight. The precipitates from this invention possess large surface areas (400-600 m²/g), and are much less sensitive on contact with water than the materials reported in References 12 and 13. The material was tested for hydrotreating reactions.

A 1978 Nalco patent [16] describes a procedure for preparing large-pore (>100 Å) aluminum phosphate materials. It consists of precipitating the material from an aqueous solution containing at least one water–soluble, inorganic aluminum salt ($Al_2(SO_4)_3$) and at least one water-soluble inorganic salt of an acid of phosphorous ((NH_4) H_2PO_4) using an alkaline aqueous solution of a water-soluble inorganic aluminate ($Na_2O.Al_2O_3$ + NaOH), followed by filtration, drying, purification, and calcination. The patent mentions that the material can be used, in conjunction with Group VI and Group VIII transition metals or zeolites, in petroleum refining operations. An example is given of using this material as a catalyst support to prepare a desulfurization catalyst.

A 1989 Dow patent [17] claims a process for preparing amorphous, porous metallo phosphates. The metals include Al, Ti, Ba, Zr, Hf, Ta, Cr, Mo, W, Mg, Sc, Cu, Fe and La or their mixtures. The phosphates have an average pore size from about 5 to about 50 Angstroms. The materials are claimed to be useful as catalysts and catalyst supports.

Several W. R. Grace patents [18] disclose a method for preparing aluminum phosphate with high porosity and phosphorous-to-aluminum ratios of approximately 1.0. The material is prepared by neutralizing an acidic aqueous solution containing aluminum and phosphorus salts to form a gel, followed by soaking and washing with a basic solution, exchanging with an organic oxygenate and drying. The compositions can be used as cracking catalysts, supports for ethylene polymerization catalysts, adsorbents, etc. The composition containing chromium was tested to the polymerization of ethylene.

Aluminum phosphate-based materials, i.e., supported and mixed aluminum phosphate, have also been prepared through non-precipitation routes. An aluminum phosphate catalyst can be prepared by impregnating γ -alumina with 58% phosphoric acid, followed by drying and calcination at 300-400°C [10]. The loading of P₂O₅ on the alumina ranges from 10 to 20%. This material is used as a dehydration catalyst.

Mixed alumina-aluminum phosphate can be prepared by incorporating PO_4 -ions into alumina or its precursor [19]. The material is prepared by impregnating a dried gel-type alumina powder with a water-soluble, phosphate-containing compound, i.e., phosphoric acid or ammonium phosphate, followed by extruding, drying, and calcination. The phosphate content ranges from 1 to 10%.

A 1975 patent [20] claims a surface-stabilized active alumina and the process for making the material. The material is prepared by incorporating in a pseudoboehmitic alumina from about 1% to about 20% by weight PO_4 -ions. Incorporation can be accomplished during the preparation of the pseudoboehmitic alumina or by addition to freshly prepared pseudoboehmitic alumina.

This literature review shows that aluminum phosphate is not a well-defined material. The sensitivity of the properties of the material to the preparation procedures provides flexibility in creating the desired material. However, as shown throughout this report, it also makes reproducibility a difficult task. Also note that none of these materials (as well as those in the open literature) was aimed at dehydrating methanol into DME under single-step, syngas-to-DME conditions. Therefore, there is a lack of prior knowledge on how to make this material for our application. The theme of this work was to identify the desirable material properties for our LPDME application and the ways to control them.

Acknowledgements

This work is a joint effort between Air Products' Reaction Technology group and a catalyst group in the company's Industrial Chemical Technology division. Gene Parris and Paula Battavio prepared all aluminum phosphate samples and brought to the project their invaluable knowledge of aluminum phosphate material.

2. EXPERIMENTAL

2.1. Life Test Experiments

Performance of the aluminum phosphate catalyst samples was evaluated under LPDME conditions. All experiments were carried out in 300 cc stainless steel autoclave reactors using the same conditions and procedures. In all runs, 8 grams of BASF S3-86 methanol synthesis catalyst and 2 grams of an aluminum phosphate sample were slurried in 120 grams of a hydrocarbon oil (Drakeol 10) and charged to the reactor. The methanol catalyst in this mixture was reduced in situ using 2% H₂ in N₂ and a standard temperature ramp (about 24 hours from ambient temperature to 240°C). Syngas was introduced to the reactor at the end of the reduction ramp. A syngas that simulates the composition of the syngas from a Shell gasifier was used throughout this study (referred to as Shell gas hereafter). It contained 30% H₂, 66% CO, 3% CO₂, and 1% N₂. The reaction temperature, pressure and gas hourly space velocity (GHSV) were 250°C, 750 psig, and 6,000 mol/kg-hr, respectively. The duration of the runs ranged from 150 to 934 hours on syngas stream.

The schematic of the reactor system is shown in Figure 2. The carbon trap was used to remove the known catalyst poisons, iron and nickel carbonyls, from the syngas before it entered the reactor. The gas liquid separator immediately connected to the reactor exit served to condense the evaporated slurry oil and return it to the reactor. The reactor pressure was controlled by the back pressure regulator (BPR). The composition of the reactor feed and effluent was analyzed via gas chromatograph. A combination of two GCs allowed analysis of the main gases (CO, H₂, CO₂), the organics (DME, methanol, other oxygenates and light hydrocarbons) and water. The inlet and exit flow rates were measured by a wet test meter. Therefore, each data point consisted of a full mass balance using all experimentally measured quantities. The mass balances for C, H, and O normally closed within two percentiles of 100 percent.



Figure 2: The Schematic of the 300 cc Autoclave Reactor System

There are three main reactions under LPDME conditions, namely

Methanol synthesis:	$2H_2 + CO \Leftrightarrow CH_3OH$	(1)
Methanol dehydration :	$2CH_3OH \Leftrightarrow CH_3OCH_3 (DME) + H_2O$	(2)
Water gas shift:	$CO + H_2O \Leftrightarrow CO_2 + H_2$	(3)

Reactions (1) and (3) are catalyzed by the methanol catalyst, and Reaction (2) is catalyzed by the dehydration catalyst. As discussed above, both methanol synthesis and methanol dehydration catalysts deactivate simultaneously under LPDME conditions due to the detrimental interaction between the two catalysts. Therefore, the performance of an aluminum phosphate catalyst sample was evaluated by four criteria: 1) dehydration activity, 2) dehydration catalyst stability, 3) methanol synthesis catalyst stability and 4) methanol equivalent productivity.

Dehydration activity is expressed in terms of the dehydration rate constant, k_d , calculated from the rate expression below:

$$R_{d} = k_{d} f_{MEOH}^{a3} / f_{H2O}^{b3} / f_{DME}^{c3} (1 - app_{d})$$
 [mol/kg-cat./hr] (4)

where f stands for fugacity in units of atm, and *appr*. is the approach to reaction equilibrium. The stability of the dehydration catalyst was evaluated by the decreasing rate of the dehydration rate constant, normalized by its initial value, with time on stream. The stability of the methanol catalyst was used as a criterion because it is an indication of the negative effect of a dehydration catalyst on the methanol catalyst through the detrimental interaction. This stability was measured by the decreasing rate of the methanol synthesis rate constant, k_m , normalized by the initial value, with time on stream. The methanol synthesis rate constant was calculated using the kinetic model, as shown below:

$$R_{m} = k_{m} f_{H2}^{a1} f_{CO}^{b1} (1 - app_{m})$$
 [mol/kg-cat./hr] (5)

The methanol equivalent productivity was defined as the moles of methanol plus two times the moles of DME produced per kilogram of catalyst per hour. It measures the overall performance of the catalyst system.

A dual catalyst system containing 8 grams of the BASF S3-86 methanol catalyst and 2 grams of Catapal B γ -alumina was used throughout this work as a reference point for both activity and stability. This is the catalyst system that was initially selected for the LPDME process, but showed unsatisfactory stability [1].

2.2. Catalyst Preparation

A typical preparation consisted of the following steps. First, an aqueous solution (premix) containing an aluminum salt (e.g., $Al(NO_3)_3$) and phosphoric acid (H_3PO_4) was prepared. A base solution (e.g., NH_4OH) was added to the premix to precipitate aluminum phosphate to a selected final pH. The precipitate was filtered with or without an aging period. The filter cake

was washed with a solvent (e.g., water), followed by drying at 110°C and calcination at elevated temperature (e.g., 750°C) in a muffle oven. The standard ramping rate was 10°C/min. The aluminum-to-phosphorous ratio (Al/P) was mainly controlled by the Al:P ratio in the premix. Because the properties of an aluminum phosphate sample were sensitive to the preparation parameters and procedures, the details will be provided when a specific sample is being discussed.

3. STABLE AIPO₄-CONTAINING DUAL CATALYST SYSTEMS

3.1. Stable Results

Our previous studies [2,3] have shown that the simultaneous deactivation of the methanol synthesis and methanol dehydration catalysts under LPDME conditions is due to detrimental interaction between the two catalysts. The most probable mechanism is the migration of Cu-and/or Zn-containing species from the methanol catalyst to the dehydration catalyst. The methanol catalyst deactivates in this process due to the loss of its active components. The migrating species arrive at the acid sites on the dehydration catalyst, deactivating the catalyst. Based on this mechanism, we started screening different dehydration materials, hoping to find a material that had dehydration activity, but little affinity to the migrating species. However, prior to aluminum phosphate, of the 29 dehydration materials we tested, none exhibited stable performance [2].

The very first aluminum phosphate sample we tested showed promise. It was an old sample from an earlier Air Products project (Sample # 7461-030.060). This sample was tested along with the BASF S3-86 methanol catalyst under LPDME conditions. The results are shown in Figures 3 and 4, along with those from a catalyst system containing 80 wt % of the same methanol catalysts and 20 wt % of γ -alumina. Figure 3 shows that the alumina phosphate was extremely stable at both 250 and 270°C. In fact, its activity increased gradually with increasing time on stream. However, the activity of this catalyst was very low, about one tenth of that of the γ -alumina.



Figure 3: Dehydration Rate Constant as a Function of Time On Stream

Figure 4 shows that the methanol catalyst in this system was not stable, deactivating at a rate similar to that in the γ -alumina-containing dual catalyst system. In spite of the unstable performance of the methanol catalyst and the low activity of the dehydration catalyst, we felt that additional attention should be given to aluminum phosphate for the following two reasons. First, this was the first time we had seen a stable dehydration catalyst under LPDME conditions, and the deactivation of the two catalysts was not related. Second, aluminum phosphate has moderate acid strength and can contain a high population of Lewis acid sites. These were the properties we then believed would mitigate the detrimental interaction between the two catalysts.

Figure 4: Methanol Synthesis Rate Constant as a Function of Time On Stream



The promise was fulfilled when we tested the next aluminum phosphate sample (#1407x1-1x1 or AP01), freshly prepared. Figure 5 displays the activity of the aluminum phosphate (k_d) as a function of time on stream. Also plotted in the figure are the results from the γ -alumina-containing dual catalyst system under the same conditions. It can be seen that the rate constant increased with time on stream initially, and leveled off at 200 hours on stream. The final activity was 35% of that of γ -alumina. This was a significant increase compared to the first sample. The sample also had remarkable stability; no deactivation was observed during the run.





The methanol catalyst in this system also exhibited good stability. Figure 6 shows that the methanol synthesis rate constant decreased with time on stream, but at a rate much slower than that for the γ -alumina-containing dual catalyst system. In fact, the deactivation rate, 0.032% hr⁻¹ was not any greater than that observed in the lab LPMEOH runs using the methanol catalyst only (ranging from 0.042 to 0.053% hr⁻¹). This indicated that the deactivation of the methanol catalyst in this system was determined by its intrinsic stability. There was no detrimental interaction between the two catalysts, which we had seen in other dual catalyst systems.



Figure 6: Normalized Methanol Synthesis Rate Constant as a Function of Time

Figure 7 depicts methanol equivalent productivity as a function of time on stream. Productivity increased with time on stream in the first 200 hrs, remained constant for the next 200 hrs, and then started to decrease. This variation is a reflection of the initial increase in dehydration activity and the constant decrease in methanol synthesis activity. Initially, the drop in methanol synthesis activity was over-compensated by the gain in dehydration activity, resulting in an overall gain in productivity. However, as dehydration activity leveled off, it could no longer offset the loss in methanol synthesis activity. At that point, deactivation of the methanol catalyst began to affect productivity. On average, a productivity of about 24.5 gmol/kg-hr of methanol equivalent was observed in this 655 hour run, a value that was about 81% of the initial productivity of the γ -alumina-containing dual catalyst system. However, the productivity of the current catalyst system surpassed that of the γ -alumina-containing dual catalyst system at 100 hours on stream due to its better stability. Furthermore, this productivity is 58% higher than a LPMEOHTM run under the same reaction conditions. The carbon-based DME selectivity from this run at 510 hours on stream was 74%, lower than that from the γ -alumina-containing dual catalyst system (95%).





In summary, this catalyst system has an acceptable activity and excellent stability. There is no detrimental interaction between the methanol catalyst and the aluminum phosphate catalyst. The stability of this catalyst system is limited by the intrinsic stability of the methanol catalyst.

Our ensuing efforts were to optimize the aluminum phosphate catalyst, namely, maximizing its activity without jeopardizing the stability of the catalyst system. The details of this effort are covered in the next section. Figures 8 to 10 show the best results we obtained from an aluminum phosphate sample denoted as AP05 (Sample 1427x1-1x1). As shown in Figure 8, the catalyst exhibited good dehydration stability and activity, with the dehydration rate constant around 7.8 after the induction period. Figure 9 shows that the rate of methanol catalyst deactivation was within the range of deactivation in lab LPMEOH runs. Methanol equivalent activity as high as 28 mol/kg-hr was observed, which was 94% of the initial activity of the γ -alumina-containing dual catalyst system (Figure 10). The CO₂-free DME carbon selectivity of this catalyst system was 80%, compared to 93% with the γ -alumina-containing dual catalyst system.

Figure 8: Methanol Dehydration Rate Constant as a Function of Time On Stream



Figure 9: Normalized Methanol Rate Constant as a Function of Time On Stream





Figure 10: Methanol Equivalent Productivity as a Function of Time On Stream

3.2. Preparation of Aluminum Phosphate Samples with Good Activity and Stability

The following six different preparations have resulted in aluminum samples that showed adequate dehydration activity and led to stable catalyst performance. These samples are denoted as AP0*, where * is a sequential number. The parameters and procedures involved in preparing one of the samples, AP05, have become our standards. AP05 has been replicated many times in the lab using the standard procedures and following the details of the operation closely.

AP01. The sample was prepared by dissolving 150 grams of Al(NO₃)₃.9H₂0 in 1125 ml of deionized H₂O, then adding 46.13 grams of 85% H₃PO₄ and stirring the mixture well. Separately, 141.75 grams of NH₄OH (28-30%) were added to 300 ml of de-ionized H₂O. The NH₄OH solution was added slowly over a period of 15 minutes to the aluminum phosphate solution to a final pH of 9.3. The precipitate obtained was filtered, and then the recovered solid was redispersed *in 300 ml of isopropanol* and filtered dry. The solid was further dried at 110°C and calcined at 650°C in an oven. The analyzed sample had an Al/P atomic ratio of 1.09.

AP02. The sample was prepared by dissolving 150 grams of Al(NO₃)₃.9H₂0 in 1125 ml of deionized H₂O, then adding 46.13 grams of 85% H₃PO₄ and stirring the mixture well. Separately, 141.75 grams of NH₄OH (28-30%) were added to 300 ml of de-ionized H₂O. The NH₄OH solution was added slowly over a period of 15 minutes to the aluminum phosphate solution to a final pH of 9.0. The precipitate obtained was filtered, and then the recovered solid was redispersed in 300 ml of de-ionized H₂O and filtered dry. The solid was further dried at 110°C and calcined at 650°C in an oven. The analyzed sample had an Al/P atomic ratio of 1.22. **AP03.** The sample was prepared by dissolving 300 grams of $Al(NO_3)_3.9H_20$ in 750 ml of deionized H₂O, then adding 30.75 grams of 85% H₃PO₄ and stirring the mixture well. Separately, 141.75 grams of NH₄OH (28-30%) were added to 300 ml of de-ionized H₂O. The NH₄OH solution was added slowly over a period of 15 minutes to the aluminum phosphate solution to a final pH of 9. The precipitate obtained was filtered, and then the recovered solid was redispersed in 300 ml of de-ionized H₂O and filtered dry. The solid was further dried at 110°C and calcined at 650°C in an oven. The analyzed sample had an Al/P atomic ratio of 3.07.

AP04. The sample was prepared by dissolving 160 grams of $Al(NO_3)_3.9H_20$ in 750 ml of deionized H₂O, then adding 30.75 grams of 85% H₃PO₄ and stirring the mixture well. Separately, 141.75 grams of NH₄OH (28-30%) were added to 300 ml of de-ionized H₂O. The NH₄OH solution was added slowly over a period of 15 minutes to the aluminum phosphate solution to a final pH of 9.2. The precipitate obtained was filtered, and then the recovered solid was redispersed in 300 ml of de-ionized H₂O and filtered dry. The solid was further dried at 110°C in an oven. Fifteen grams of the dried sample were re-dispersed and filtered an additional two times, each in 300 ml of de-ionized H₂O. The recovered solid was further dried at 110°C and calcined at 650°C in an oven. The analyzed sample had an Al/P atomic ratio of 1.64.

AP05. The sample was prepared by dissolving 160 grams of $Al(NO_3)_3.9H_20$ in 750 ml of deionized H₂O, then adding 30.75 grams of 85% H₃PO₄ and stirring the mixture well. Separately, 141.75 grams of NH₄OH (28-30%) were added to 300 ml of de-ionized H₂O. The NH₄OH solution was added slowly over a period 15 minutes to the aluminum phosphate solution to a final pH of 9.2. The precipitate obtained was filtered, and then the recovered solid was redispersed in 300 ml of de-ionized H₂O and filtered dry. The solid was further dried at 110°C and calcined at 750°C in an oven.

AP06. The sample was prepared by dissolving 220 grams of Al(NO₃)₃.9H₂O in 750 ml of deionized H₂O, then adding 30.75 grams of 85% H₃PO₄ and stirring the mixture well. Separately, 141.75 grams of NH₄OH (28-30%) were added to 300 ml of de-ionized H₂O. The NH₄OH solution was added slowly over a period 15 minutes to the aluminum phosphate solution to a final pH of 8.9. The precipitate obtained was filtered, and then the recovered solid was redispersed in 300 ml of de-ionized H₂O and filtered dry. The solid was further dried at 110°C and calcined at 750°C in an oven. The analyzed sample had an Al/P atomic ratio of 2.12.

The properties and performance of these samples are summarized in Tables 1 and 2, respectively.

Tuble 1. Summary of the Troperties of Selected Mummum Thosphate Samples					
Dehydration	Sample #	Measured	Surface	Pore	Median Pore
Catalyst		Al/P Ratio	Area	Volume	Diameter
			(m^2/g)	(cc/g)	(A)
AP01	1407x1-1x1	1.09	191	0.505	141
AP02	1416x1-1x1	1.22	160, 210	0.597	139
AP03	1431x1-1x1	3.07	226, 232	0.733	169
AP04	1427x1-1x3	1.64	159	n.a.	n.a.
AP05	1427x1-1x4	1.64	176	n.a.	n.a.
AP06	1429x1-1x3	2.12	n.a.	n.a.	n.a.

 Table 1: Summary of the Properties of Selected Aluminum Phosphate Samples

Table 2: Summary of the Performance of Dual Catalyst Systems Containing Different Aluminum Phosphate Samples

Dehydration	Sample #	Methanol	DME CO ₂	Stability of	Stability of
Catalyst		Equiv. Prod.	Free Carbon	Methanol	Dehydration
		(mol/kg-hr)	Selectivity	Catalyst	Catalyst
			(%)	(%k _m /hr)	
AP01	1407x1-1x1	24.6	69	0.032	Stable
AP02	1416x1-1x1	26.2	77	0.049	Stable
AP03	1431x1-1x1	28.0	78	0.038	Stable
AP04	1427x1-1x3	27.2	73	0.038	Stable
AP05	1427x1-1x4	29.1	80	0.043	Stable
AP06	1429x1-1x3	24.5	64	0.050	Stable
γ-alumina ^a		31	93	0.086 ^b	Rapid deact'n

a. Initial performance.

b. The rate of long-term deactivation.

3.3. Rate of Catalyst Deactivation as a Function of Reaction Temperature

A life run was carried out at three different temperatures, 250, 270 and 290°C. Sample AP01 was used in this experiment. Figures 11 and 12 show that the activity of both catalysts increased when temperature was raised to 270°C. However, stability was not preserved at 270°C; both catalysts deactivated rapidly. Similar fast deactivation of both catalysts was observed at 290°C (not shown).





Figure 12: Stability of the Dehydration Catalyst at Different Temperatures



The apparent activation energies for the deactivation of the two catalysts can be estimated by assuming zero-order deactivation kinetics and representing the deactivation rate by $-d(k/k_0)/dt$, where *k* is the rate constant at any time *t*, and k_0 stands for the initial rate constant at a given temperature. The results are summarized in Table 3.

Table 3:	Apparent Activation Energies for Deactivation of the Methanol Synthesis
	Catalyst (S3-86) and AP01

Catalyst Deactivation		Deactivation	Deactivation Rate at	Ea
	Rate at 250°C	Rate at 270°C	290°C	(kcal/mol)
S3-86	0.044%	0.32%	0.71%	40
AP01	0	0.24%	0.44%	90

These results show that the rate of catalyst deactivation is a strong function of reaction temperature, and the aluminum phosphate-containing dual catalyst system becomes unstable at temperatures greater than 250°C.

4. INVESTIGATION OF PREPARATION PARAMETERS

The performance of the aluminum phosphate catalyst, in terms of its activity and its effect on the stability of the methanol catalyst, is very sensitive to preparation parameters and procedures. The preparations that led to good aluminum phosphate samples have been described in the last section. This section describes our observations and understanding of the effects of important preparation parameters and procedures on the catalyst performance.

4.1. Starting Aluminum Salts

Different aluminum salts have been used in the literature for preparing aluminum phosphate as isomerization catalysts [21]. These include $Al(NO_3)_3$, $Al(SO_4)_3$ and $AlCl_3$. The aluminum phosphate prepared using $Al(SO_4)_3$ has shown greater acidity than that made from $Al(NO_3)_3$. Therefore, we prepared an aluminum phosphate sample (1412x1-1x1) using $Al(SO_4)_3$ as the aluminum precursor, instead of the standard $Al(NO_3)_3$. However, the dehydration activity of this sample was only one-half of the nominal activity of most of the samples prepared from $Al(NO_3)_3$. Furthermore, the methanol catalyst in this system was not stable. We speculated that this could be due to the residual sulfate groups in the sample. While these residual groups could serve as acid centers for pure dehydration reactions, they may enhance the detrimental interaction with the methanol catalysts under LPDME conditions, resulting in fast deactivation of both catalysts. Furthermore, they may cause additional damage to the methanol catalyst because sulfur is a known poison to the methanol catalyst. Therefore, we did not pursue this line of research with $Al(SO_4)_3$. In addition, since chlorine is also a known potent poison to the methanol catalyst, we did not pursue $AlCl_3$ as a potential aluminum precursor.

4.2. Precipitation Conditions

Final pH

The final pH in the precipitation step is a crucial parameter. Our standard final precipitation pH is 9, which produces numerous good aluminum phosphate samples. Sample 1407x4-1x1 was prepared by precipitating to a final pH of 7. This sample resulted in very poor methanol catalyst stability (-0.10%/hr) and very low dehydration activity (k_d =2.3).

Order of Addition

The order of addition in the precipitation step has a strong effect on the stability of the catalyst system. We prepared a sample according to the same procedures as those used in preparing Sample AP05. The only difference was the order of addition. That is, the aluminum phosphate solution was added slowly over a period 15 minutes to the NH₄OH solution to a final pH of 9.2. The resulting sample (1430x1-1x1) showed reasonable dehydration activity, but caused very rapid deactivation of the methanol catalyst.

4.3. Al:P Ratio

The Al:P ratio in the stoichiometric aluminum phosphate is 1:1. However, aluminum phosphate with an Al:P ratio greater than 1 can be prepared using an Al-rich starting solution. These aluminum phosphate samples are mixtures of aluminum phosphate and aluminum oxide [22]. We have tried to use this parameter to tune the activity of the aluminum phosphate catalyst. Four good aluminum phosphate samples with different Al:P ratios have been obtained from this effort: 1416x1-1x1 (AP02), 1427x1-1x4 (AP05), 1429x1-1x3 (AP06) and 1431x1-1x1 (AP03). They have Al:P ratios of 1.2, 1.6, 2.1 and 3.0, respectively.

Table 4 summarizes dehydration activity, methanol equivalent productivity, and methanol catalyst stability as a function of Al/P for these four samples. Increasing the Al:P ratio from 1.2 to 1.6 resulted in an increase in the dehydration activity from 6.8 to 7.8. This led to an increase in the methanol equivalent productivity from 26.2 to 29.0 mol/kg-hr; the latter matched the productivity from the γ -alumina-containing dual catalyst system. No further increase in dehydration activity was obtained with further increases in the Al:P ratio. The two samples with Al:P ratios of 2.1 and 3.0 actually exhibited lower activity than the sample with an Al:P ratio of 1.6. Moreover, the last two samples caused rapid deactivation of the methanol catalyst for the first 120 hours on syngas stream before the aging rate leveled off to the baseline level, as shown in Figure 13 for AP03. (The sudden drop in activity between the 5th and 6th data points was due to a system shutdown caused by a power failure.) These results demonstrate that the optimal Al:P ratio is 1.6, which became the standard ratio in our preparations.

Sample ID	Al/P Ratio	Dehydration Activity, k _d	MEOH Equiv. Prod. (mol/kg-hr)	Stability of MEOH Catalyst (slope)
1416x1-1x1 or AP02	1.2	6.8	26.2	- 0.049%
1427x1-1x4 or AP05	1.6	7.8	29.0	- 0.043%
1429x1-1x3 or AP06	2.1	6.3	26.0	-0.050%a
1431x1-1x1 or AP03	3.0	7.5	27.5	-0.038% ^a

Table 4: Catalyst Performance Versus Al/P Ratio

a: Deactivation rate after the first 120 hours on stream.

Figure 13: Normalize Methanol Rate Constant as a Function of Time On Stream



4.4. Maturing Time of the Precipitate

Sufficient time for the precipitate to mature appears to be important for obtaining a good aluminum phosphate sample. We prepared two samples from the same mother liquor (the precipitate prior to filtration). The first sample, 1427x1-4Ax1, was filtered with the vacuum connected to the filtering flask turned off, and the sample was left as a wet gel for 18 hours. The gel was dried by turning the vacuum on and then washed with water. For the second sample, 1427x1-4Dx1m (AP05D), the mother liquor was deliberately slurried (or matured) for 24 hours prior to filtration and water wash. Both samples were dried at 120°C followed by calcination at 750°C in air.

The life test results of these two samples are listed in Table 5. Since the samples exhibited an induction period in which the activity increased with increasing time on stream, the rate constant

at 150 hours on stream was chosen to keep the comparison on a consistent basis. The table shows that Sample 1427x1-4Ax1 resulted in poor methanol catalyst stability. In contrast, the sample with 24 hours of maturing time, 1427x1-4Dx1, led to a methanol catalyst stability that was similar to the lab LPMEOH baseline. This suggests that maturing time is a very important factor.

Sample ID	Name	LPDME run	Rate of Deact. of S3-86, (%/hr)	k _d at 150 Hours On Stream
1427x1-		15198-62	0.12	6.7
4Ax1				
1427x1-	AP05	15695-28	0.047	6.2
4Dx1	D			

Table 5: LPDME Results from Catalyst Systems Containing Different AlPO₄ Samples

Note that the "vacuum off, wet gel" method yielded good samples (e.g., AP05). In addition, the extra maturing provided by this slow filtration had been thought to be the difference between the resulting good samples and the poor samples from fast filtration with vacuum on. Yet, Sample 1427x1-4Ax1 did not produce good methanol catalyst activity. We believe that, as important as the maturing step is, slow filtration is not a good way to control it. This may explain the poor reproducibility between Sample 1427x1-4Ax1 and previous good samples. A dedicated maturing step appears to be more helpful.

This position is supported further by the following preparation. A sample (1468x1-1x1 or AP07) was prepared by maturation for 7 days before filtration. This was a larger preparation (200 grams compared to <50 grams in other preps), and the concentration of the starting solution was higher than that of other preparations by a factor of two. Before that time, we did not have success with large preparations having concentrated starting solutions. However, Sample AP07 gave a dehydration rate constant of 6.6 and stable methanol catalyst performance. A similar preparation (1443x1-1x1), but one without the maturing period, showed poor performance.

4.5. Washing Procedures

Iso-Propanol vs. Water

In preparing our first successful aluminum phosphate sample (#1407x1-1x1 or AP01), we used iso-propanol to wash the precipitate. This posed a safety problem for large-scale production because the regent is flammable. Therefore, we tried another preparation using procedures similar to those for AP01, except that the precipitate was washed with water. As shown in Figures 14 to 16, the resulting sample (#1416x1-1x1 or AP02) exhibited greater dehydration activity than AP01. The methanol catalyst in this system had a slightly faster deactivation rate than the system containing AP01 (Fig. 15). However, this difference was within the range of experimental error; the deactivation rate we have observed from lab LPMEOH runs ranges from 0.042 to 0.053% hr⁻¹. The methanol equivalent productivity of this system, after the induction period, was 6% higher than the AP01-containing system (Fig. 16). The analysis showed that the two different washing solvents resulted in significantly different properties between AP01 and AP02, such as surface area and Al:P ratio (Table 1). Because of the positive results from AP02 and the obvious safety and economical advantages, water became our standard washing reagent.



Figure 14: Methanol Dehydration Rate Constant as a Function of Time On Stream



Figure 15: Normalized Methanol Synthesis Rate Constant as a Function of Time On Stream

Figure 16: Methanol Equivalent Productivity as a Function of Time On Stream



Washing Scheme

Thorough washing of the filter cake can be the difference between a good and a poor aluminum phosphate sample. However, washing alone does not guarantee a good sample.

Extra washing can have positive effects on the performance of an aluminum phosphate sample. In one instance, we prepared two samples with an Al/P ratio of 1.64. For the first one (1427x1-1x3 or AP04), the filter cake was washed with water two additional times after it had been dried at 110°C. For the other one (1427x1-1x1), no such additional wash was used. The first sample led to stable methanol catalyst performance, while the second one did not.

However, extra washing did not result in a stable methanol catalyst in other instances. Samples 1432x1-1x4 and 1442x1-1x2 were prepared by washing the filter cake three times, instead of the single wash in the standard preparation. Sample 1442x1-1x6 was prepared by an additional wash of a sample prepared by the standard procedures. The methanol catalyst stabilities of all three samples were negatively affected; the deactivation rates were 0.061%, 0.11%, and 0.11% hr⁻¹, respectively.

4.6. Calcination Temperature and Ramp Rate

A calcination temperature equal to or greater than 650°C is needed to produce a good aluminum phosphate sample. However, calcination at high temperatures alone does not guarantee a good sample.

Samples 1407x1-1x3 and 1407x1-1x1 (AP01) were taken from the same batch. The only difference was the lower calcination temperature for Sample #1407x1-1x3 (450°C) than for Sample 1407x1-1x1 (650°C). Figure 17 shows that the sample with the lower calcination temperature had greater dehydration activity. However, it led to unstable performance of the methanol catalyst (Fig. 18).

Figure 17: Dehydration Activity and Stability of Different Aluminum Phosphates



Figure 18: Methanol Synthesis Stability of the Catalyst Systems Containing Different Aluminum Phosphates



Some of our good aluminum phosphate samples were prepared by calcination at 650°C (AP01, AP02, AP03 and AP04). Others required higher calcination temperatures, e.g., 750°C for AP05 and AP06. Calcination at even higher temperatures resulted in lower dehydration activity, while having little effect on stability.

As stated earlier, high temperature calcination alone does not guarantee a good aluminum phosphate catalyst. Sample 1442x1-1x3 was prepared by final calcination at 750°C, but it gave poor stability to the methanol catalyst. In practice, 750°C has been used as our standard final calcination temperature.

Catalyst performance also depends on the rate of the heating ramp. Sample 1416x1-1x4 was prepared from the same dried filter cake as Sample 1416x1-1x1 (AP02). The only difference was the rate of the heating ramp during the calcination procedure: $2^{\circ}C$ for Sample 1416x1-1x4 and $10^{\circ}C$ for Sample 1416x1-1x1. While Sample 1416x1-1x1 yielded good catalyst stability, Sample 1416x1-1x4 caused a very large initial deactivation of the methanol catalyst, followed by rapid deactivation of both catalysts. This pair of experiments led us to use $10^{\circ}C$ as our standard ramping rate.

4.7. Post Treatment: Nitridation

Aluminum phosphate can be treated with ammonia at elevated temperatures to form oxynitride through O and N exchange [23]. The goal is to introduce basic sites into aluminum phosphate. This scheme was investigated in our application as a post-treatment step to convert poor aluminum phosphate samples into good ones.

The starting sample (1427x1-2x1) used in this investigation was among the poorest aluminum phosphate samples we have made. It caused the methanol catalyst to deactivate at 0.14% per hour, as shown in Figure 19. This sample was treated at 800°C under flowing NH₃ (90%, N₂ balance) for several hours. The nitrided sample gave good methanol catalyst stability (0.046% per hour). However, the dehydration activity of the aluminum phosphate suffered from the nitridation treatment; the dehydration rate constant decreased from 8 to 6.



Figure 19: Methanol Catalyst Stability with Different Aluminum Phosphate Samples

We tried nitridation on another poor aluminum phosphate sample (1443x1-1x1). The treated sample (1443x1-1x2) had a surface nitrogen content of 2.3 at.%. Nitridation reduced the aging rate of the methanol catalyst by a factor of 2. However, nitridation decreased the dehydration rate constant from 8.6 to 6.0. Further nitridation decreased dehydration activity more without additional benefit to methanol catalyst stability.

4.8. Aluminum Phosphate in Supported Form

We prepared two supported aluminum phosphate samples for our LPDME applications by doping γ -alumina with phosphoric acid to incipient wetness, followed by drying and calcination at 650°C. This method has been used in preparing aluminum phosphate catalysts for dehydration and isomerization [10]. Sample 1 (1423x1-1x1) and Sample 2 (1424x1-1x1) had different aluminum phosphate loadings, 3 and 25 wt %, respectively. Figures 20 and 21 show the performance of these two samples against γ -alumina and AP01. The dehydration activity of Sample 1 was similar to that of the γ -alumina-containing catalyst system. The aging pattern for the Sample 1-containing dual system also closely tracked that of the γ -alumina-containing system. In other words, the lower loading sample essentially behaved like γ -alumina.





Figure 21: Methanol Synthesis Rate Constant as a Function of Time On Stream



At high loading (25 wt %), the doped sample behaved more like bulk aluminum phosphate (e.g., AP01) in terms of dehydration activity. However, the stability of both methanol synthesis and dehydration catalysts in this system was poor.

The parametric study discussed above demonstrates that the performance of an aluminum phosphate catalyst is very sensitive to the preparation details. Good parameters have been observed for each step and have become part of our standard preparation procedures. These include: 1) using Al(NO₃)₃ as the Al precursor, 2) adding NH₄OH to aluminum nitrate and phosphoric acid solution for precipitation, 3) controlling the final precipitation pH at 9, 4) providing adequate maturing time, 5) providing a thorough water wash, and 6) calcinating at greater than 650°C temperatures. We also observed that post-nitridation treatment can convert a poor sample to a good one. However, this is accomplished at the sacrifice of dehydration activity. The optimal Al:P ratio is 1.6. The bulk form is better than the supported form.

5. MECHANISTIC DISCUSSION

We have developed two hypotheses to explain the sensitivity of the performance to preparation or why one sample is better than the other.

5.1. Hypothesis 1: Uniformity

The first hypothesis is based on the uniformity of the aluminum sample or how well the aluminum and phosphorous is mixed in the finishing sample. If not well mixed, the sample may contain a separate phosphoric oxide phase or subgrains. These small subgrains may have negative effects on methanol catalyst stability, as discussed below. Therefore, uniformity is essential for a good aluminum phosphate sample.

This uniformity hypothesis can explain why certain preparation procedures are important. Uniform precipitation will be key in producing a good starting material. The right order of addition, proper final pH and vigorous agitation all become crucial for achieving a uniform precipitate. However, precipitation is a very rapid process and is difficult to control. Therefore, it may contribute greatly to poor reproducibility from one preparation to another. The ensuing procedures may also affect the uniformity of an aluminum sample. Maturing may provide the time for the precipitate to become a more uniform structure. Calcination at high temperatures may also increase mobility of the species inside the framework for better uniformity.

The uniformity hypothesis assumes that the subgrains of phosphoric oxide are the source of instability of the methanol catalyst. Hydroxyl groups can be formed on the surface of the subgrains in the presence of water under LPDME conditions. These surface hydroxyl groups then serve as the receptive sites for Cu- or Zn-containing species migrating from the methanol catalyst, therefore, causing the methanol catalyst to deactivate. This hypothesis is supported by the following rehydration experiment.

An aluminum phosphate sample (1443x1-1x1) was treated with water-saturated N₂ at 300°C for 48 hours. TGA results showed that a significant amount of water evolved when the treated sample was heated above 250°C. This indicates that OH groups were formed in the aluminum

phosphate during the steam treatment. (The physically absorbed water desorbs between 100 and 150° C.) This steam-treated sample (1443x1-1x5) was used along with the S3-86 methanol catalyst in a standard LPDME run using Texaco gas. It caused rapid initial deactivation of the methanol catalyst (0.26% per hour) before the aging slowed to 0.16% per hour. This initial deactivation rate was much greater than that of the original aluminum phosphate (1443x1-1x1) without the steam treatment (0.19% per hour). This observation, along with the TGA data, indicates that a higher OH concentration in aluminum phosphate will cause more rapid deactivation of the methanol catalyst.

The surface hydroxyl groups may also be the reason why high-temperature calcination and postnitridation treatment improve methanol catalyst stability; both remove surface hydroxyl groups from a poor sample. Aluminum phosphate is iso-structural to silica gel. It is well known that a fully dehydrated silica surface is hydrophobic and difficult to rehydrate [24]. Calcination at high temperatures in our preparation may also serve to remove the surface hydroxyl groups from the phosphoric oxide subgrains and make rehydration difficult. Therefore, high-temperature calcination can sometimes convert poor aluminum phosphate samples to good ones.

Nitridation is known to remove the surface hydroxyl groups by substituting –OH groups with –NH₂ [23]. The reaction changes the surface structure of phosphoric oxide and makes rehydration difficult under LPDME conditions. This may explain why nitridation converts poor aluminum phosphate samples into good ones.

5.2. Hypothesis 2: Contamination

This hypothesis assumes that poor preparations will produce loosely bound phosphorouscontaining species in the sample. These "loose species" may be mobile under LPDME conditions and poison the methanol catalyst. The "toxicity" of phosphorous toward the methanol catalyst is not documented in the literature to our knowledge. However, the element immediately below P in the periodic table, As, is a known potent poison to the methanol catalyst. In brief, this hypothesis assumes that if an aluminum phosphate sample is not properly prepared, it becomes a source of contamination to the methanol catalyst.

This hypothesis can also explain the effects of some preparation parameters on the performance of the aluminum phosphate catalyst. Precipitation again can be crucial in not producing any loose species in the first place. Maturing may provide the time for the loose species to bind to and become part of the aluminum phosphate framework. Thorough washing may remove the loose species. High-temperature calcination and post-nitridation treatment may either evaporate the loose species or fix them permanently to the framework.

Efforts have been made to verify this hypothesis. Several good and poor aluminum phosphate samples were mixed well in water and boiled for several hours. The specimens were then cooled, and solids were allowed to settle out. The water in the clear top layer of the specimens was analyzed for phosphorous. However, no difference in phosphorous was seen between the good and poor samples. Therefore, this result does not provide evidence for the contamination hypothesis; however, it does not rule out the hypothesis either, since the species may not be loose or soluble in water below 100°C, but may be mobile under LPDME conditions.

Both hypotheses can explain our observations in the preparation sensibility study; they are two alternative explanations and do not contradict each other. In fact, if one assumes that the phosphoric oxide subgrains are the source of the loose species, the contamination hypothesis becomes equivalent to the uniformity hypothesis. Therefore, we have used either or both of these hypotheses to guide our preparation study and materials scaleup [25], although neither is rigorously proven.

VII. SUMMARY AND RETROSPECT

Amorphous aluminum phosphate can serve as the methanol dehydration catalyst in the dualcatalyst system for the single-step liquid phase syngas-to-DME process. The material is prepared by precipitating a solution containing Al(NO₃)₃ and H₃PO₄ with NH₄OH, followed by washing, drying and calcination. This catalyst has adequate dehydration activity and good stability, and it can co-exist with the Cu-based methanol synthesis catalyst without negative effects on the synthesis catalyst's stability. However, aluminum phosphate catalyst performance is very sensitive to the details of the preparation. Poor preparations would give samples that cause the methanol synthesis catalyst to deactivate rapidly under LPDME conditions.

In this study, the parameters for each preparation step were investigated, and a set of the best parameters and procedures was identified. Six different good aluminum phosphate samples and their replicas were prepared in the lab. The sensitivity to preparation can be explained by two hypotheses. One hypothesis assumes that the surface hydroxyl groups on a non-uniformly formed sample cause the methanol catalyst to deactivate. The other assumes that a poor aluminum phosphate sample contains loose species that poison the methanol synthesis catalyst under LPDME conditions. This information has been used to scale up the material [25].

Aluminum phosphate is the first dehydration material that has given us stable and productive LPDME performance. It demonstrated the technical viability of the LPDME process and kept the catalyst R&D efforts moving forward. The stable baseline provided by the aluminum phosphate-containing dual-catalyst system allowed us to recognize the role of reaction conditions on catalyst deactivation in the LPDME process and to identify stable operating domains for the process [26]. This understanding eventually brought more cost-effective and commercially available γ-aluminum back to the LPDME process [27].

REFERENCES

- 1. B. L. Bharat, Synthesis of Dimethyl Ether and Alternative Fuels in the Lquid Phase from Coal-Derived Synthesis Gas, Topical Report prepared for DOE by Air Products and Chemicals, Contract No. DE-AC22-90PC89865, September 1992.
- X. D. Peng, An Investigation of the Cause and Mechanism of Catalyst Deactivation, Topical Report prepared for DOE by Air Products and Chemicals, Inc., Contract No. DE-FC22-94 PC93052, February 2000.
- 3. X. D. Peng, B. A. Toseland and R. P. Underwood, Stud. Surf. Sci. Catal. 111 (1997) 175.
- 4. U.S. Patent 4,341,069 to Mobil Oil Corp. (1982).
- 5. U.S. Patent 4,423,155 to Mobil (1983).
- 6. A. C. Safianos and M. S. Scrurrel, Ind. Eng. Chem. Res. 30 (1991) 2372.
- 7. G. Cai et al., Applied Catal. A 125 (1995) 29.
- 8. K. L. Ng, Ph. D. Thesis, Imperial College of Science, Technology and Medicine, March 1999.
- 9. J. B. Moffat, Catal. Rev. Sci. Eng. 18 (1978) 199. (Phosphate as catalysts).
- 10. "Catalyst Manufacture Laboratory and Commercial Preparation," A. B. Stiles (ed.), Marcel Dekker, Inc., New York, 1983.
- 11. K. Tanabe, M. Misono, Y. Ono and H. Hattori, "New Solid Acids and Bases: Their Catalytic Properties," Elsevier, New York 1989.
- 12. U.S. Patent 3,342,750 (1967).
- 13. U.S. Patent 3,904,550 (1975).
- 14. U.S. Patent 4,080,311 (1978).
- 15. U.S. Patent 4,233,184 (1980).
- 16. U.S. Patent 4,066,572 (1978).
- 17. U.S. Patent 4,845,069 to the Dow Chemical Company (1989).
- 18. U.S. Patents 5,030,431 (1991), 5,292,701 (1994), Re. 34,911 (1995) and EP Patent 215,336 (1992).
- 19. U.S. Patent 3,969,273 (1976).
- 20. U.S. Patent 3,879,310 (1975).
- 21. J. M. Campelo, A. Garcia, D. Luna and J. M. Marinas, J. Catal. 111 (1988) 106.
- 22. J. M. Campelo, A. Garcia, D. Luna, J. M. Marinas and M. I. Martinez, *Materials Chem. Phys.* **21** (1989) 409.
- 23. A. Massinon, J. A. Odriozola, Ph. Bastians, R. Conanec, R. Marchand, Y. Laurent, P. Grange, *Appl. Catal. A: General* **137** (1996) 9.
- 24. R. K. Iler, "The Chemistry of Silica," John Wiley & Sons, New York 1979.
- 25. A. W. Wang, Scaleup of Aluminum Phosphate Catalyst for Pilot Plant LPDME[™] Run, Topical Report, Air Products and Chemicals, Inc., Contract No. DE-FC22-94 PC93052, January 2002.
- 26. X. D. Peng, Topical Report in preparation for DOE by Air Products and Chemicals, Inc.
- 27. B. L. Bhatt, B. A. Toseland, X. D. Peng and E. C. Heydorn, Symposium on "C₁ Chemistry," 17th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 11-15, 2000.